

PROCESS MODIFICATIONS FOR DESILICATION OF KRAFTGREEN LIQUOR

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in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY**

**By
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CERTIFICATE

It is certified that this work ' PROCESS MODIFICATIONS OF DESILICATION OF KRAFT GREEN LIQUOR DURING CAUSTICIZATION' has been carried out under my supervision and that has not been submitted elsewhere for a degree.

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~~Signature~~

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NOMENCLATURE

A	Clarifier cross section, m^2
C_L	Arbitrary concentration of lime mud at height Z_i , Kg/m^3
C_O	Slurry concentration of lime mud at height Z_O , Kg/m^3
C_u	Underflow concentration of lime mud, Kg/m^3
D	Diameter, m
F	Kg of stage I liquor/kg of lime mud in feed to clarifier
G	Specific gravity of lime mud
k	Constant in kiln design equation
L	Length, m
M	Factor representing angle of repose of lime sludge in kiln
N	Speed of rotation, rpm
S	Specific gravity of stage I liquor
S_s	Specific gravity of thickened slurry
T	Retention time, h
t	Temperature, $^{\circ}C$
tpd	Tons per day of pulp production
U	Kg of stage I liquor/kg of lime mud in underflow from clarifier
V	Volume, m^3
V_L	Settling velocity of lime mud, cm/h
Z	Height of solid-liquid interface in settling test, cm.
Z_i	Height of solid-liquid interface in settling test at time, t_i , cm.
Z_O	Initial height of slurry in settling test, cm
θ	Angle of inclination of kiln, degree
$\bar{\rho}_{av}$	Average density of the slurry, Kg/m^3
ρ	Density of the stage I liquor, Kg/m^3

ABSTRACT

Two thirds - three fourths of silica in kraft green liquor ($6-12 \text{ g SiO}_2/\text{l}$) can be removed from the chemical recovery system of a bamboo kraft pulp mill by a two step causticizing operation. The first stage requires 25-30 per cent of total lime to remove 65-75 per cent of silica in green liquor and is carried out at $95-100^\circ\text{C}$, and 90-100 min. Lime sludge containing 8-30 per cent SiO_2 from this stage is discarded. Causticizing reactions are completed in the second stage, ^{with} the balance of lime, at 100°C and 90 min with an overall causticization of 80 per cent and producing lime sludge containing 3-4 per cent SiO_2 . The latter can be calcined in a kiln and reused. The results are illustrated by applying the techniques developed to a 250 tpd bamboo kraft pulp mill. A preliminary cost estimates giving a fixed capital investment of Rs.50,00,000 and saving Rs.15 per ton of pulp, favour further development of work on pilot plant scale in a paper mill.

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CHAPTER 1

INTRODUCTION

Silica enters the chemical recovery system in a paper mill through fibrous raw materials like bamboo (1-2.5 per cent SiO_2), bagasse (1-2 per cent SiO_2), and grasses (2-15 per cent SiO_2) and also through lime (2-10 per cent SiO_2) used for causticization of the green liquor. Silica tends to deposit as a hard scale in digester and evaporators and also forms beehive deposits in recovery furnace. These scales tend to reduce both thermal efficiency and chemical recovery besides increasing maintenance problems.

The general range of concentration of silica (as SiO_2) in the various liquor streams in a bamboo kraft pulp mill is indicated below: weak black liquor (3-12 g/l), strong black liquor (7-45 g/l) green liquor (9-14 g/l) and white liquor (0.5-2.9 g/l)[1]. Silica will be present in these streams mainly as dissolved sodium silicate. Silica balance for a 250 tons/day bamboo kraft pulp mill is given in Fig.1-1. Sodium silicate in green liquor will form calcium silicate during causticization and the lime sludge produced will contain 5-20 per cent SiO_2 . Since lime sludge containing more than 5-6 per cent SiO_2 cannot be calcined efficiently it is commonly disposed off as a solid waste from the pulp mill.

Methods for the removal of silica from weak black liquor or green liquor are based either on acidification or lime addition.

Idrees [2] has reviewed the available literature on desilication of pulp mill liquors, has studied desilication of kraft green liquor by carbonation using flue gas, Fig. 1-2. Carbonation techniques for desilication necessitate fairly elaborate equipment thereby increasing both capital and operating costs.

This investigation is based on the concept of carrying out causticization of green liquor in two stages. In the first stage bulk of the silica 60-80 per cent will be removed by adding the requisite amount of lime (about 30 per cent) and the lime sludge thus obtained containing 10-15 per cent silica will be disposed off. The causticization reactions are completed in the second stage with the balance of lime. Lime sludge from this second stage will contain less than 4 per cent SiO_2 and calcination can be done satisfactorily in a rotary kiln or a fluidized bed calciner.

A block diagram of the proposed process is given in Fig. 1.3. This study deals with desilication efficiency of both laboratory and commercial green liquor using reagent grade lime as well as commercial lime. Major variables studied during desilication of green liquor include, lime charge, reaction time, temperature and concentration of the

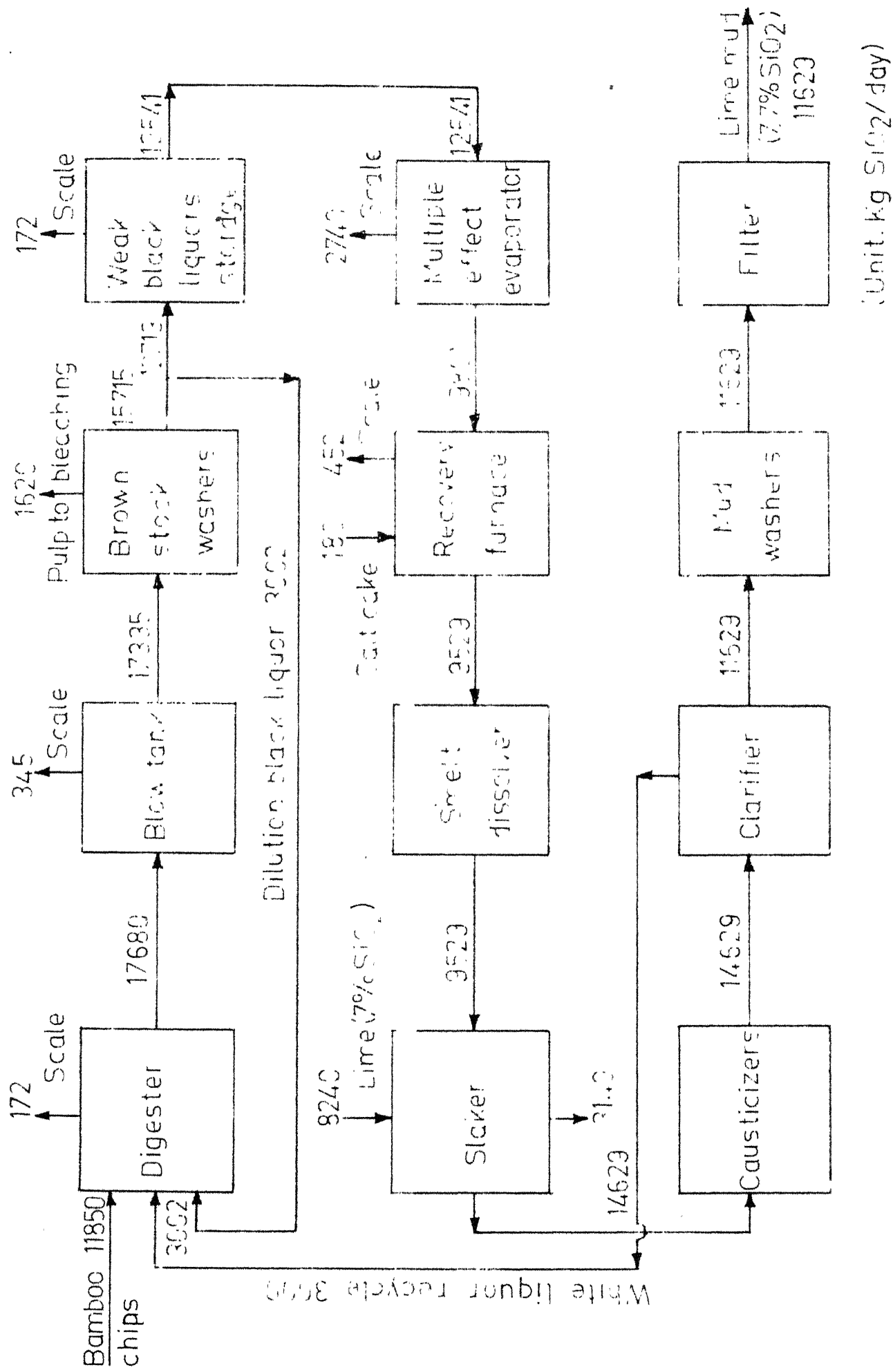


Fig. 1.1 -Silica balance for conventional 250 TPD bamboo kraft pulp mill

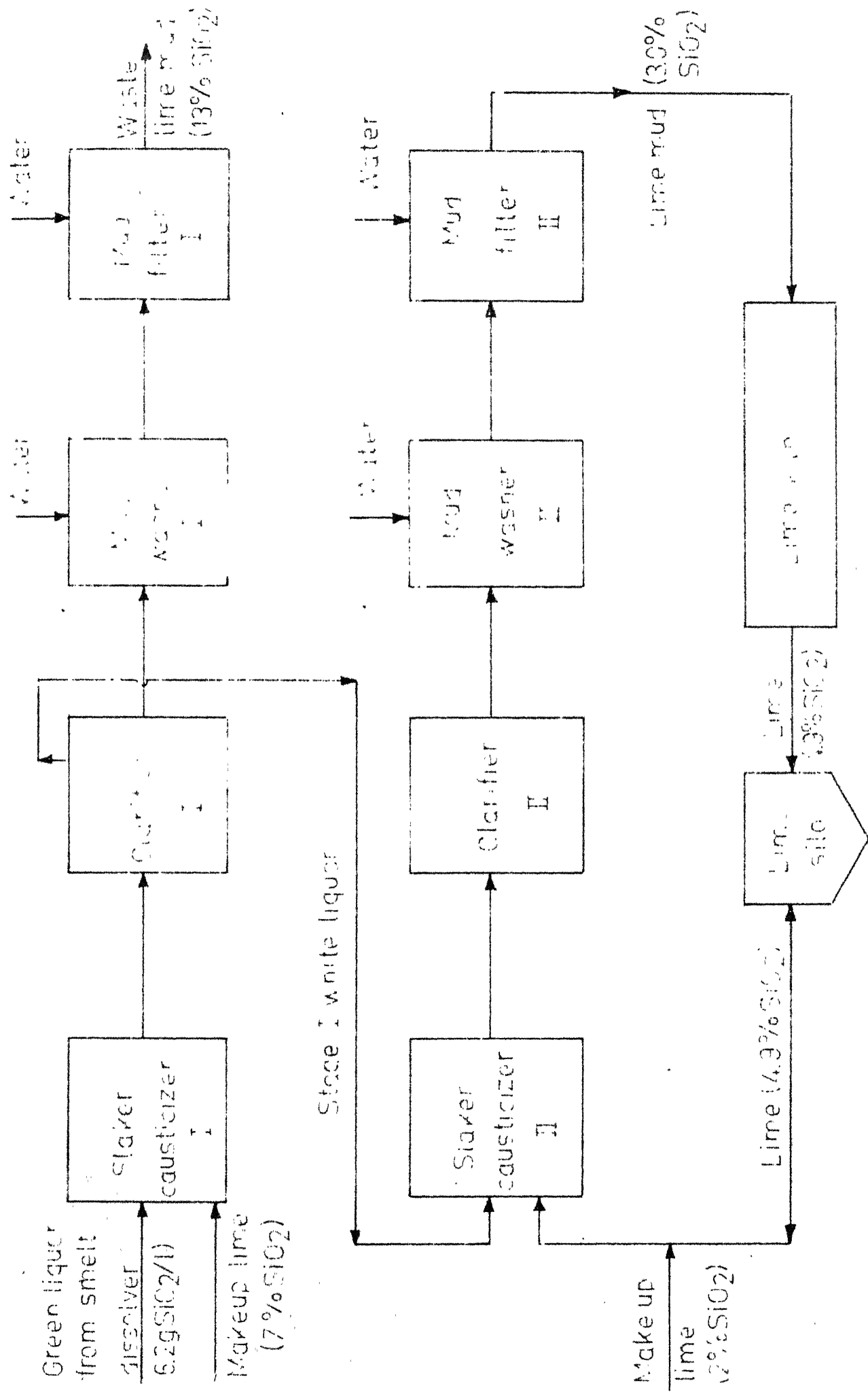


Fig. 1.3 - Proposed modification in causticization for desilication of green liquor.

silica in green liquor. Techniques developed in this work are illustrated by incorporating a two stage causticization treatment for the green liquor during chemical recovery operations of a 250 tpd bamboo kraft pulp mill.

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CHAPTER 2

EXPERIMENTAL INVESTIGATIONS OF GREEN LIQUOR DESILICATION DURING CAUSTICIZATION

Experimental investigations of this work deal with the influence of reaction time, temperature and lime dosage on desilication efficiency of green liquor during causticizing in two stages. Experiments are performed with both laboratory and commercial green liquors.

The composition of the green liquor samples (laboratory and commercial) used for the various experiments is given in Table 2.1. Laboratory green liquor was used for experiments 1-43 and commercial green liquor was used in experiments 44-67. Reagent grade lime was used for experiments with laboratory green liquor and commercial lime from a pulp mill was used for the experiments with commercial green liquor.

The effects of variations of reaction time (15-90 min.) and lime addition (10-100 per cent) on desilication of the green liquor containing (8.1 g SiO_2 /l) were studied in this work. The results on desilication efficiency, causticization efficiency, and silica in lime mud are given in Tables 2.2 to 2.5. Tables 2.2A to 2.5A report the results of stage I causticizing and Tables 2.2B to 2.5B correspond to the second stage of causticizing experiments. A typical laboratory study of two stage causticization is shown in Fig. 2.1. The

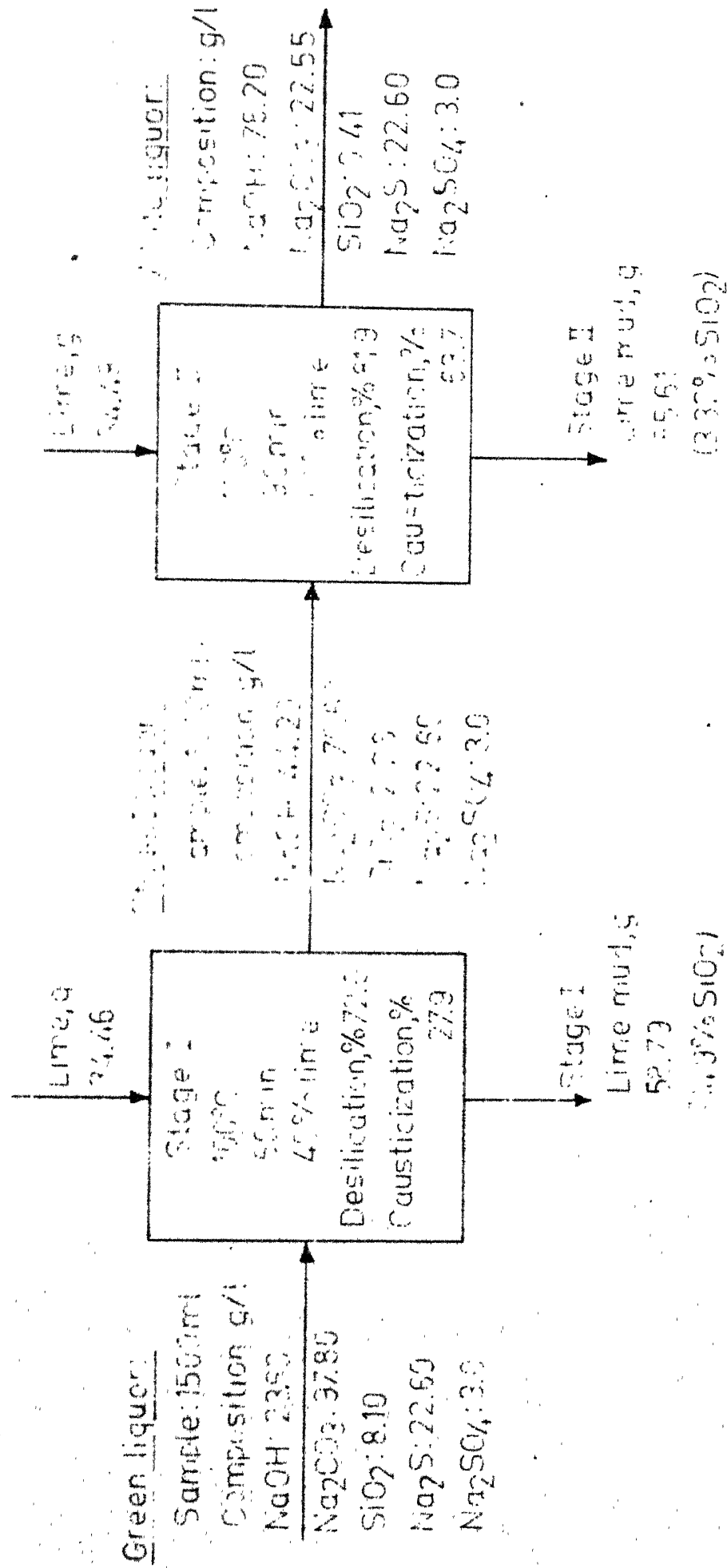


Fig.2.1 - Typical laboratory study of two stage causticization

effect of temperature (60-100°C) on desilication of the laboratory green liquor is given Table 2.6 to 2.8 and the results are graphically correlated in Fig. 2.6.

The sample of commercial green liquor received from the mill contained 3.4 g SiO_2 /l and the results of runs 44 to 58 relate to this sample, Table 2.9 to 2.11 correspond to these runs. The concentration of silica in commercial green liquor was increased to 10.5 g SiO_2 /l by the addition of requisite amount of sodium metasilicate and was used for runs 59-67. The results of these desilication experiments are summarised in Table 2.12. Experimental studies cover the range of 3-11 g SiO_2 /l for the kraft green liquor.

DISCUSSIONS:

Figure 2.2 shows the effect of lime charge and reaction time in stage I on desilication efficiency of laboratory green liquor with 8.1 g SiO_2 /l, at 100°C. As the lime dosage in stage I is increased from 10 to 100 per cent, the desilication efficiency increases from 30 to 97 per cent at 100°C, 90 min. Upto 40 per cent of lime charge the increase in desilication efficiency is sharp. For 30 per cent lime charge at 100°C, as the reaction time is increased from 15 to 90 min. the desilication efficiency increases from 51 to 66 per cent. Increase in reaction time, increases the silica content of lime mud in stage I. For 30 per cent lime charge, 100°C, as the reaction time is increased from 15 to 90 min.,

silica in lime mud increases from 15 to 15.8 per cent. Increase in lime addition from 10 to 100 per cent decreases silica content of lime mud from 18.9 to 8.4 per cent in stage I, at 100°C , 90 min.

Figure 2.3 represents the effect of lime charge and reaction time in stages I and II on causticization efficiency of laboratory green liquor at 100°C . Increase in lime addition from 10 to 100 per cent increases the causticization efficiency from 10.5 to 78 per cent at 100°C , 90 min. in stage I. As the reaction time is increased in stage I from 15 to 90 min, the partial causticization efficiency increases from 13 to 22 per cent. Causticization efficiency in stage II decreases as the lime addition is decreased. For 90 min., 100°C , decrease in lime addition from 90 to 25 per cent in stage II decreases the causticization efficiency from 71 to 61 per cent. Increase of reaction time from 15 to 90 min. in stage I, increases the causticization efficiency in stage II from 52 to 62 per cent for 50 per cent lime charge, 100°C . Figure 2.4, shows the effect of reaction time (in stage I), and lime charge in stage I and II, on overall causticization efficiency. Increase in stage I reaction time from 15 to 90 min, increases the overall causticization efficiency from 68 to 75 per cent. ^{at 100°C , 90 min} For reaction time less than 60 min in stage I, as the lime charge is increased the overall causticization efficiency decreases. For 15 min, at

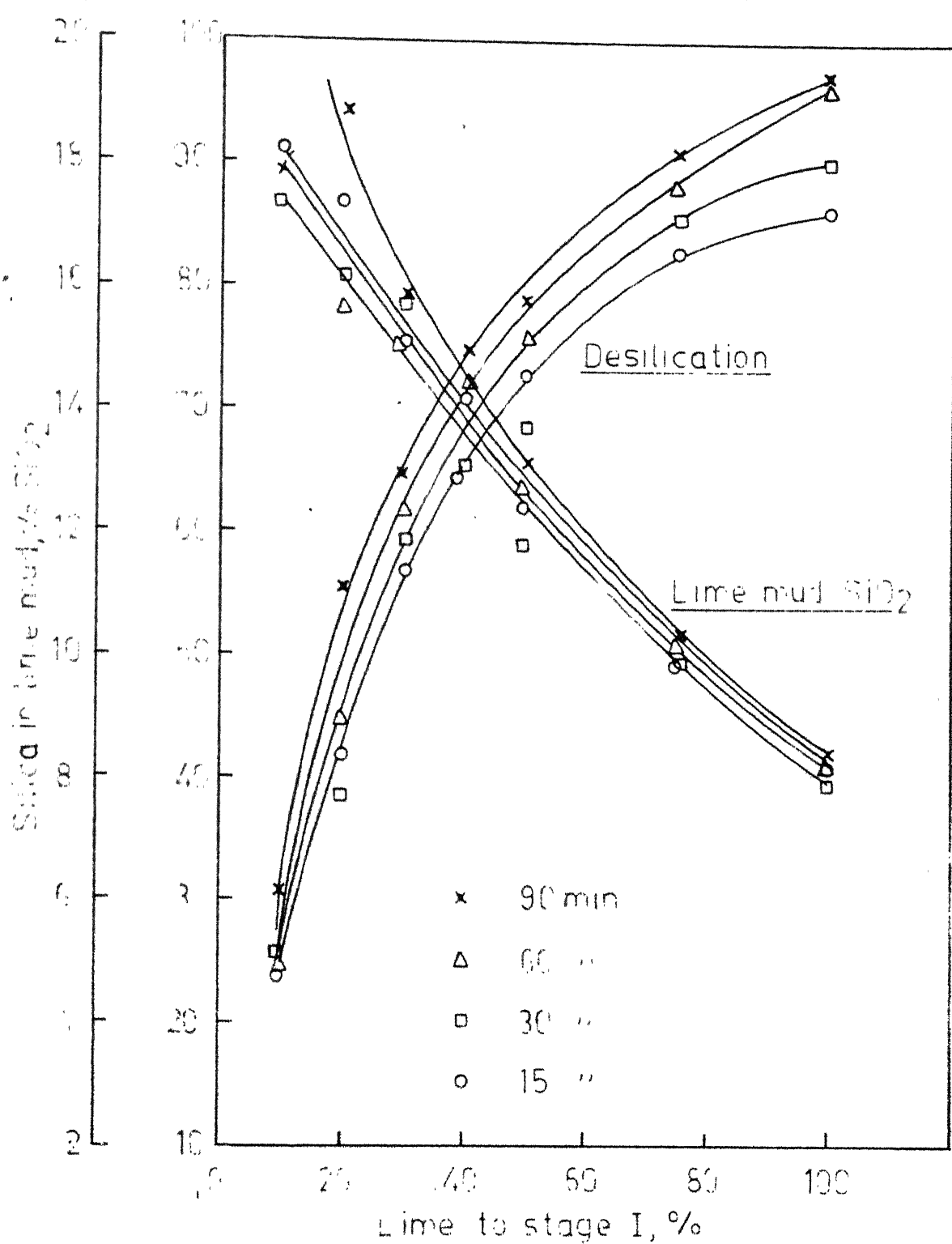


Fig. 2.2 - Effect of lime charge and reaction time in 1st stage on desilication of laboratory green liquor at 160° C.

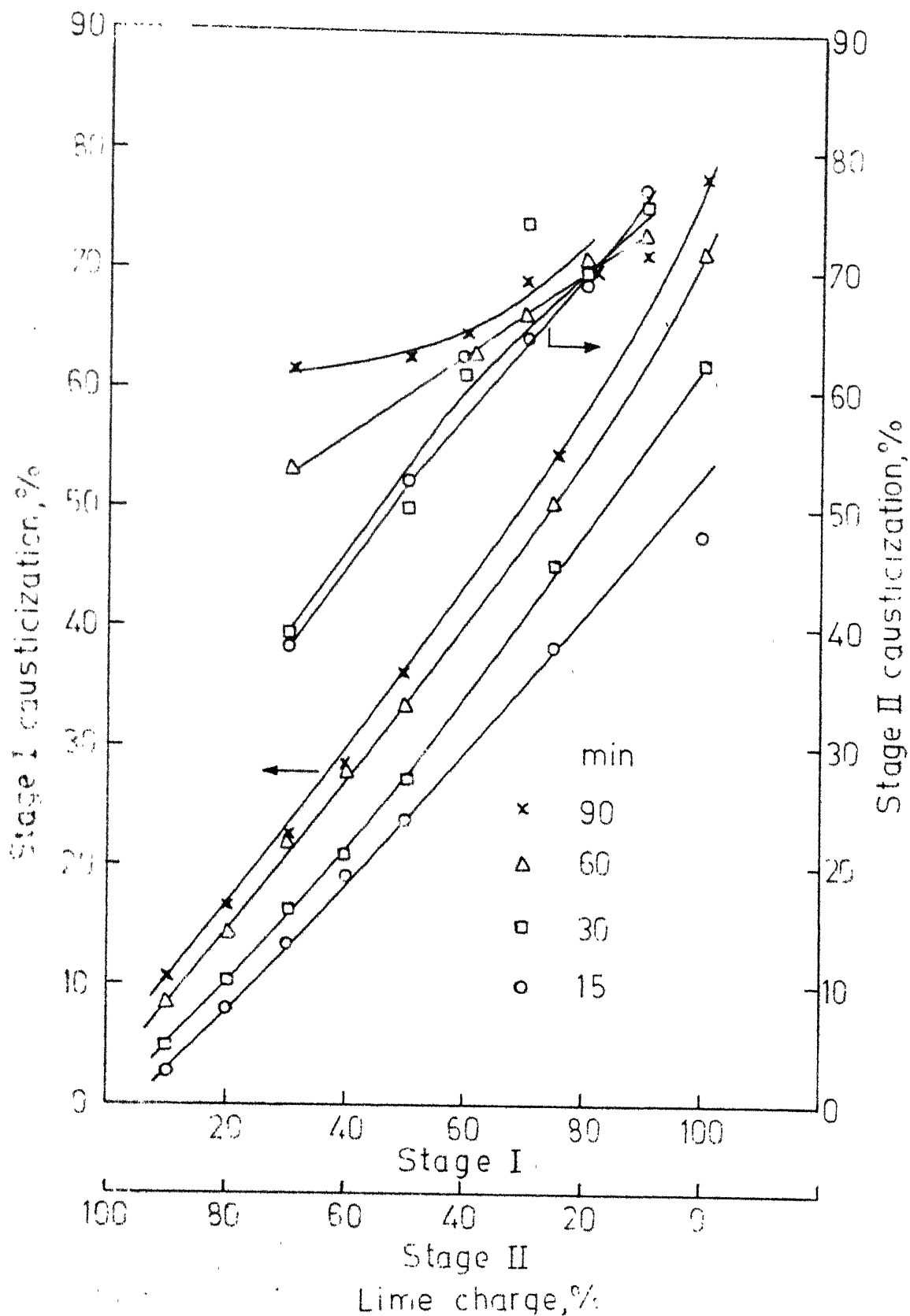


Fig. 23 - Effect of lime charge and reaction time in stages I and II on causticization efficiency at 100°C

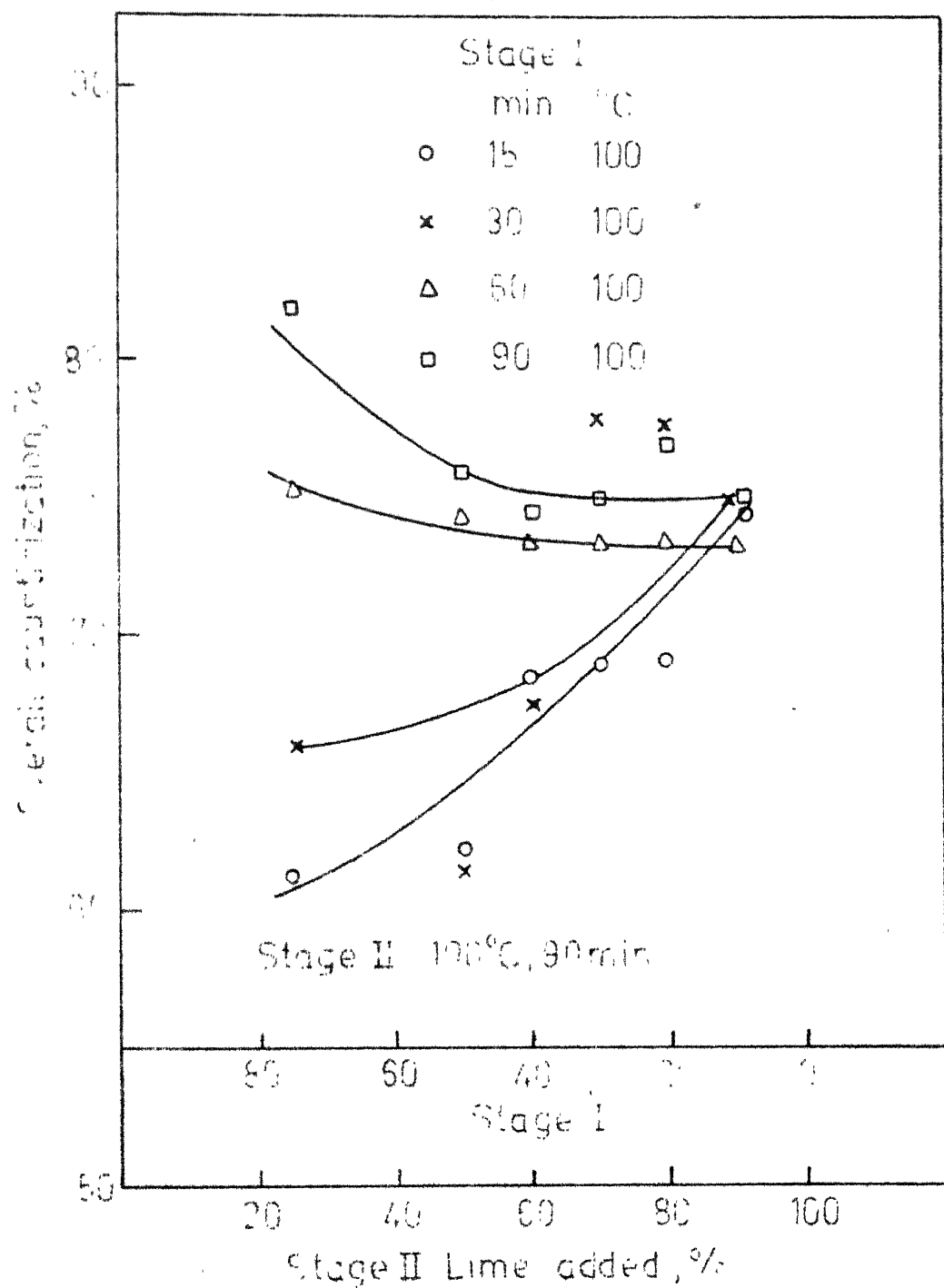


Fig 2.4 -Overall efficiency of causticization in two stages

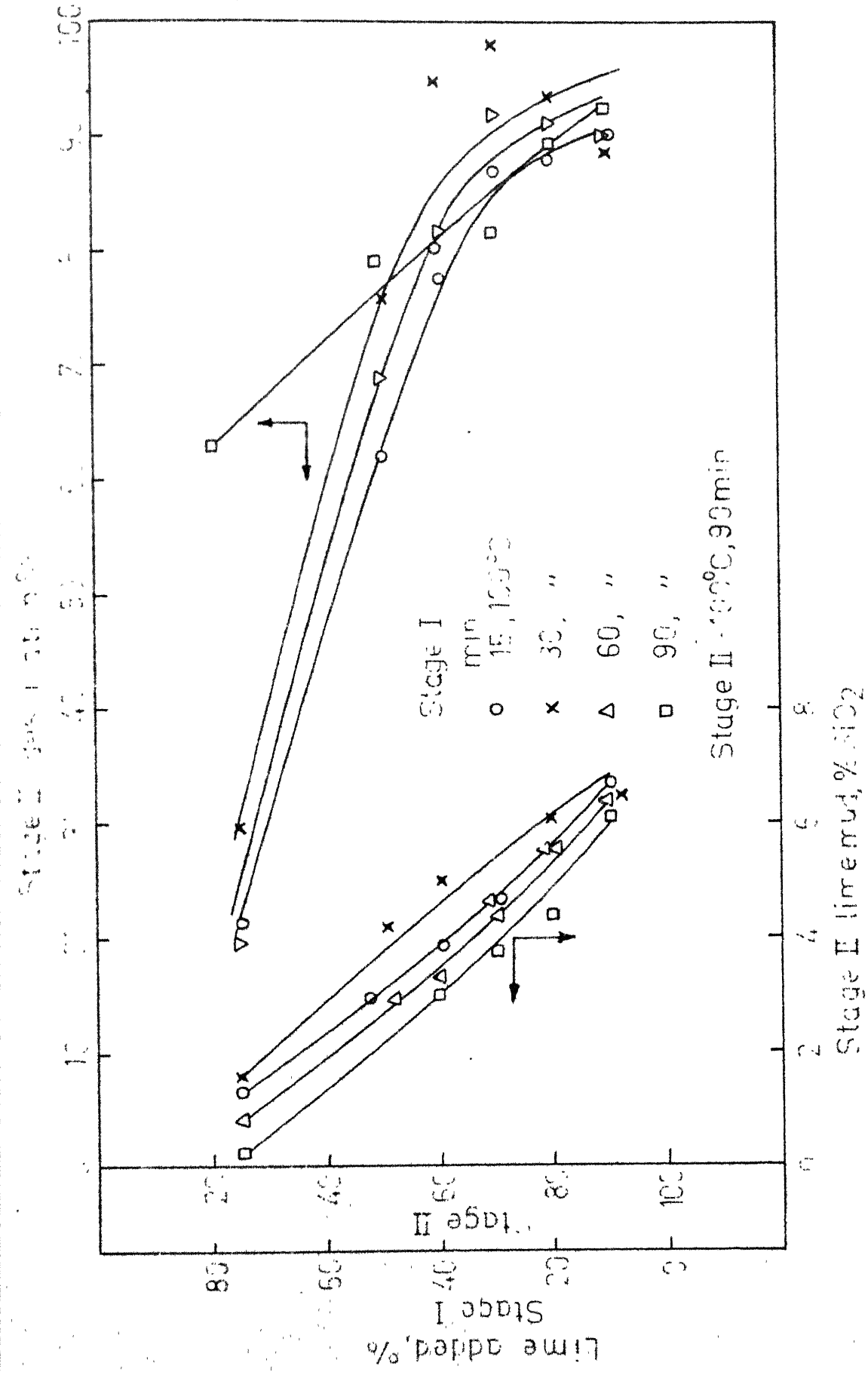


Fig 2.5 - Effect of lime charge and reaction time on desilication and silica in lime mud.

100°C, as the lime dosage is increased from 10 to 75 per cent in stage I, the overall causticization decreases from 75 to 62 per cent. But for the same lime dosage the overall causticization efficiency increases from 75 to 82 per cent, for 90 min, 100°C. Hence the reaction time in stage I should be more than 60 min.

Figure 2.5, shows the effect of lime charge and reaction time (in stage I) on desilication efficiency and silica content in lime mud in second stage. For 90 min., 100°C (in stage I) as the lime addition in stage II is decreased from 90 to 25 per cent, the desilication efficiency decreases from 92 to 63 per cent. Decrease in lime addition in stage II from 90 to 10 per cent, the silica in lime mud decreases from 6.2 to 0.2 per cent at 100°C, As the reaction time is increased from 30 to 90 min, Silica in stage II lime mud decreases from 4.6 to 3.7 per cent. Hence, high reaction time in stage I results in lower silica content in lime mud (in stage II).

Figure 2.6 shows the effect of reaction temperature in stage I on desilication efficiency and silica in lime mud. Decrease in the reaction temperature from 100 to 60°C, decreases the desilication efficiency from 78 to 61 per cent, for 35 per cent lime charge and 90 min. This is also accompanied by a decrease in the causticization efficiency from 23 to 10 per cent. Hence lower temperatures are unfavourable

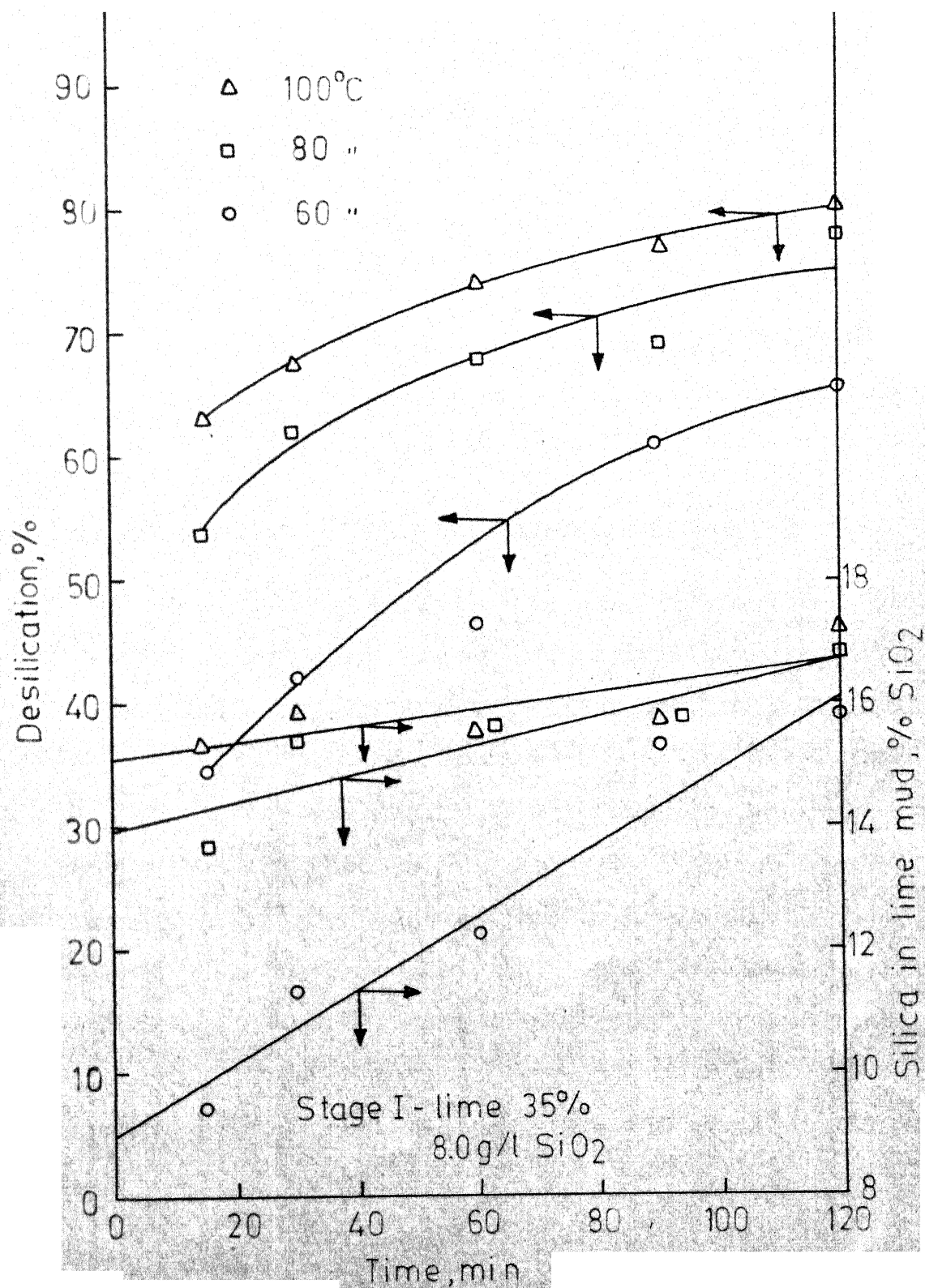


Fig. 2.6 -Effect of reaction time and temperature on desilicat of laboratory green liquor.

for both desilication and causticization efficiencies. For reaction time less than 60 min, desilication efficiency falls sharply. As the reaction time is decreased from 60 to 15 min, the desilication efficiency decreases from 74 to 63 per cent for 35 per cent lime charge and 100°C . Hence the reaction time should be more than 60 min in stage I. Decrease in reaction temperature decreases the silica content in lime mud. For 35 per cent lime addition, and 90 min, as the temperature is lowered from 100 to 60°C the silica in lime mud decreases from 15.7 to 15.3 per cent.

Figure 2.7 shows the effect of lime charge and reaction time in stage I on desilication efficiency and SiO_2 in lime mud for commercial green liquor with a silica concentration of 3.4 g/l. Here the desilication efficiency increases linearly with increase in lime charge. Increase in lime charge from 10-40 per cent increases the desilication efficiency from 11 to 41 per cent and the causticization efficiency from 13.9 to 41.0 per cent at 100°C , and 90 min. As the reaction time is increased from 30 to 90 min, the desilication efficiency increases from 29 to 53 per cent for 50 per cent lime charge, and 100°C .

Figure 2.8, represents the effect of reaction time and lime charge in stage I on desilication of commercial green liquor with 10.5 g SiO_2 /l at 100°C . Increase in lime addition and reaction time increases the desilication efficiency. For 30 min, 100°C , as the lime addition is

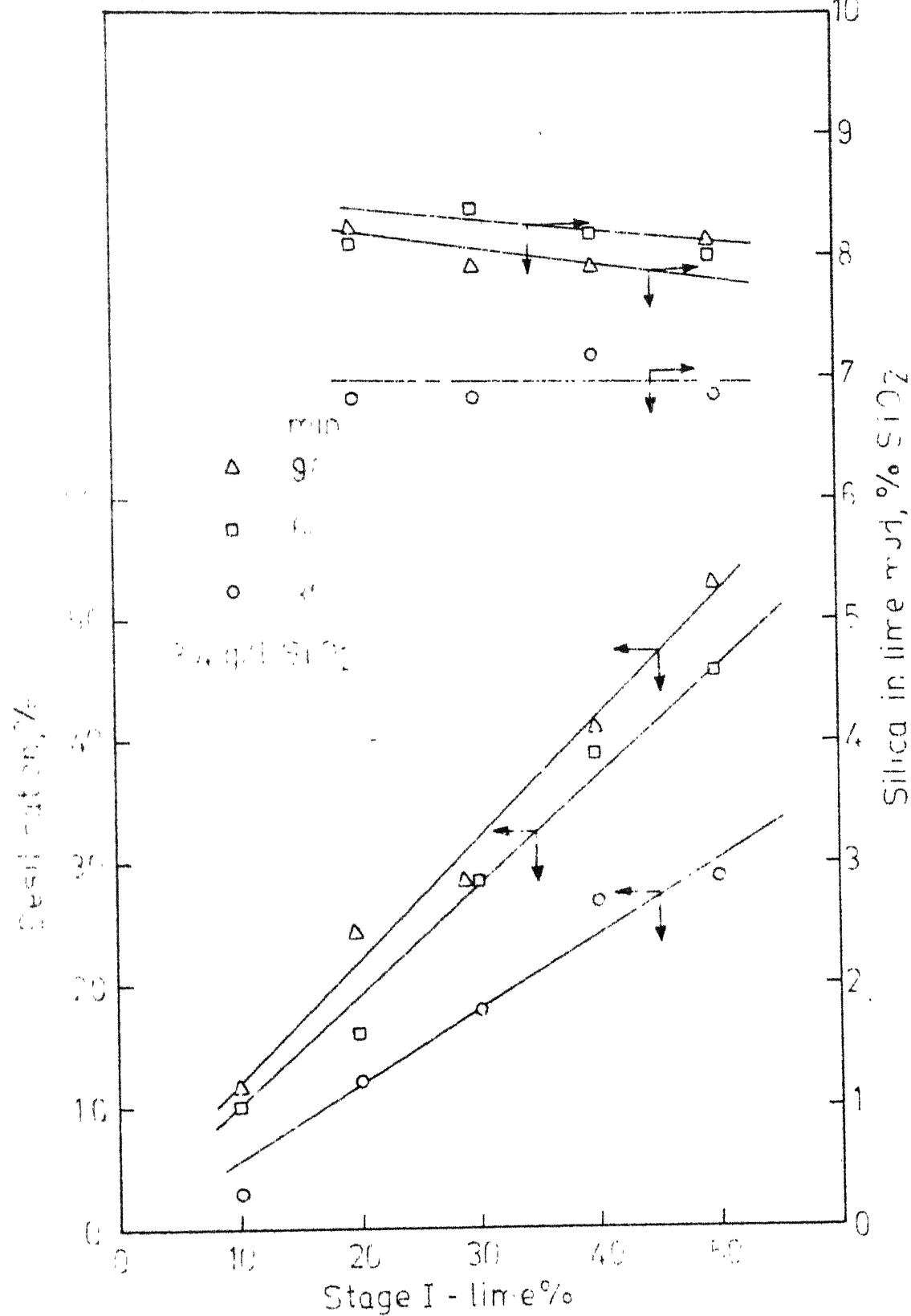


Fig 2 7-Effect of lime charge and reaction time in stage on desilication of commercial green liquor at 100°C

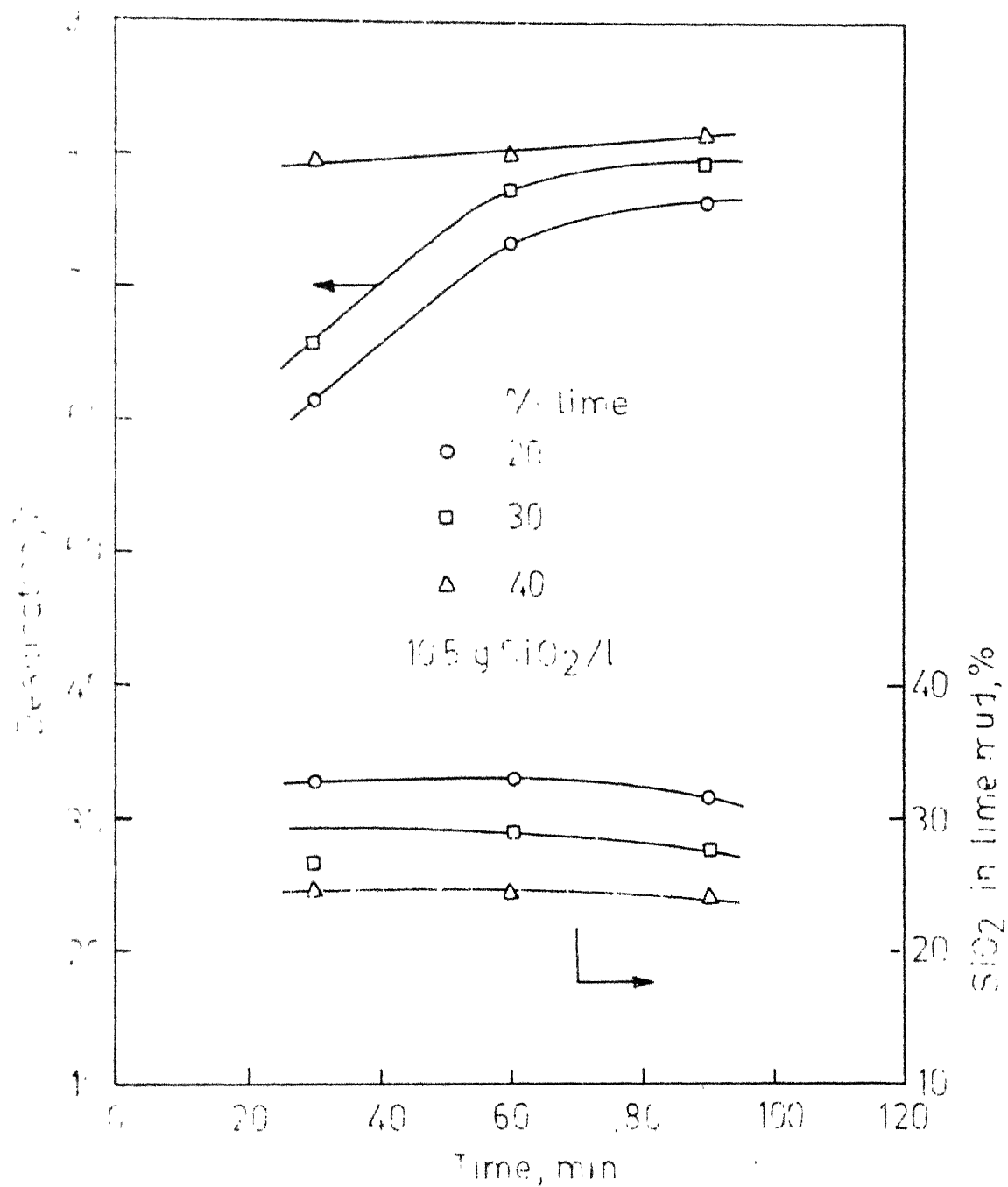


Fig. 2.5 - Effect of reaction time and lime charge on desilication of commercial green liquor at 100°C.

increased from 20 to 40 per cent the desilication efficiency increases from 62 to 80 per cent. Decrease in the reaction time from 60 to 30 min decreases the desilication efficiency from 78 to 66 per cent whereas decrease in reaction time from 90 to 60 min decreases the desilication efficiency from 79.5 to 78.0 for 30 per cent lime charge and 100°C . Hence the reaction time should be above 60 min. Increase in desilication efficiency is very sharp upto 30 per cent lime charge. Increase in lime addition from 20 to 40 per cent decreases the SiO_2 in lime mud from 33 to 24 per cent at 100°C , 60 min for commercial green liquor with 10.5 g SiO_2/l .

Figure 2.9 shows the effect of silica concentration and lime charge on desilication efficiency in stage I for commercial green liquor. At 100°C , 90 min, and 30 per cent lime charge for commercial green liquor with 3.4 g SiO_2/l and 10.5 g SiO_2/l the desilication efficiency is 29.2 per cent and 79.5 per cent, and the SiO_2 in lime mud is 7.9 per cent and 27.8 per cent, that is as the silica concentration is increased in green liquor the desilication efficiency and SiO_2 in lime mud increases.

Figure 2.10 represents the effect of silica concentration in green liquor on causticization efficiency. As the concentration of silica in green liquor is increased from 3.4 to 10.5 g/l the causticization efficiency decreases from 31 to 16 per cent at 100°C , 90 min. Figures 2.9 and 2.10

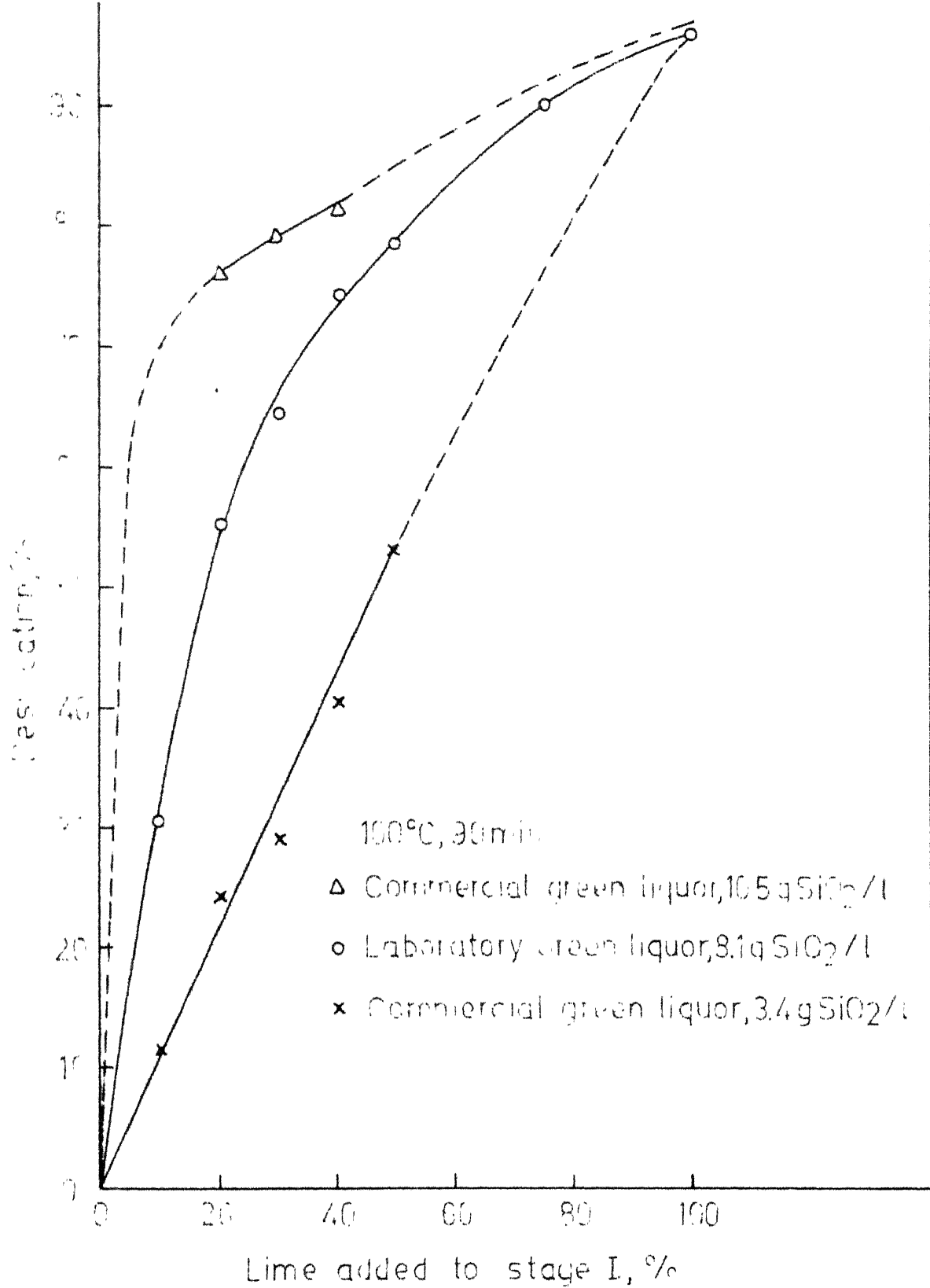


Fig. 2.9 - Effect of lime charge and silica concentration on desilication efficiency in stage I.

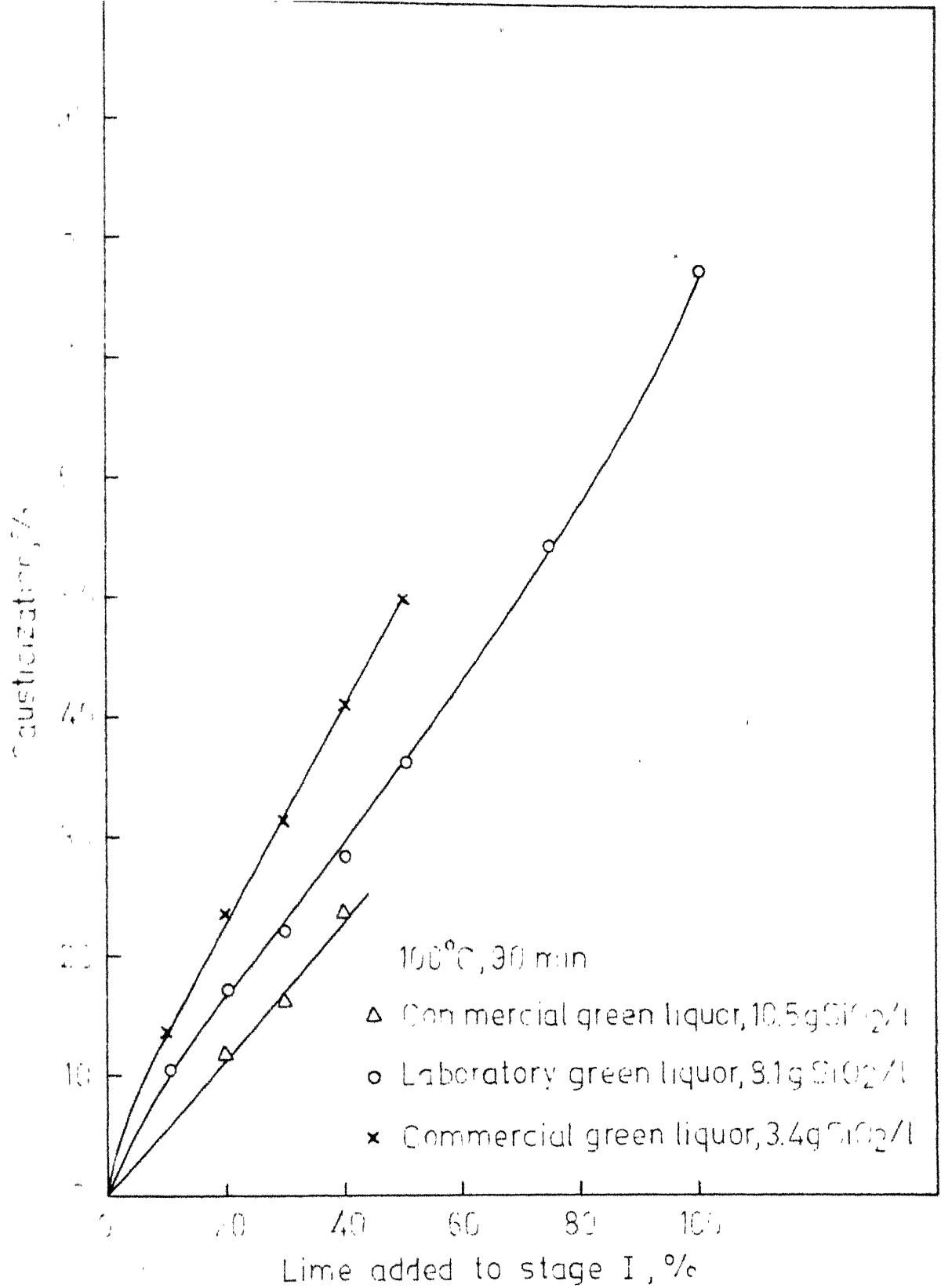


Fig. 2.10-Effect of lime charge and silica concentration on causticization efficiency in stage I.

show the behaviour of laboratory green liquor and commercial green liquors. The behaviour of desilication efficiency vs the lime charge for commercial green liquor (10.5 g SiO_2/l) is similar to that of laboratory green liquor (8.1 g SiO_2/l). For both laboratory and commercial green liquors as the lime charge, and reaction time is increased the desilication efficiency and silica in lime mud increases.

The above results indicate that the best conditions in stage I will be 90-100°C, 70-90 min, and 20-30 per cent lime charge for green liquor containing 6-12 g SiO_2/l .

For a 250 tpd bamboo kraft pulp mill green liquor will contain a silica concentration of about 6-2 g/l. The recommended conditions in stage I are 30 per cent lime charge, 90 min, 100°C to yield a desilication efficiency of about 65 per cent.

The preliminary results of Thakur and Rao [11] are in general agreement with the findings of the detailed investigations of this study.

PROPOSED PROCESS DESCRIPTION:

Green liquor from smelt dissolver is fed to the stage I slaker where 30 per cent of theoretically required lime is added. Total retention time in stage I slaker and causticizers is about 90 min and it is divided as 20 min in

slaker and 70 min in causticizers. The slurry from the slaker is pumped to two causticizers arranged in series. Product mixture from the causticizer is taken to a clarifier. The underflow from clarifier (30 per cent of solids) is fed to the mud washers to recover alkali. Two counter current thickeners (mud washers) recover alkali and the weak wash from the mud washer is sent to the smelt dissolver for dissolving the smelt. The underflow from the mud washer (40 per cent of solids) is filtered in rotary drum filter. The lime mud cake containing (10-15 per cent SiO_2) from filter (60 per cent solids) is disposed off.

The overflow from the stage I clarifier is fed to the stage II slaker where the reburned lime alongwith makeup lime is added. The total retention time in slaker and causticizers is about 120 min and it is distributed as 30 min in slaker and 90 min in causticizers. The slurry from the slaker is fed to the three causticizers in series. White liquor slurry containing lime mud is fed to the clarifier. White liquor overflow from the clarifier is recycled to the digester and the underflow (lime mud) containing 32 per cent solids is fed to stage II mud washers to recover the alkali. The weak wash from mud washer is also sent to the smelt dissolver. The underflow from mud washer (40 per cent of solids) is filtered in stage II rotary drum filter. The lime mud cake containing (3 per cent SiO_2) from the filter is fed to rotary kiln and the calcined lime (4.9 per cent SiO_2) is recycled to the slaker II.

TABLE 2.1: COMPOSITION OF KRAFT GREEN LIQUOR, g/l

Sample	Run No.	NaOH	Na ₂ S	Na ₂ CO ₃	Na ₂ SO ₄	SiO ₂
Laboratory Sample A	1-28	23.6	22.6	97.8	3.0	8.1
Laboratory Sample B	29-43	27.5	23.4	98.4	3.0	8.0
Commercial Sample A	44-58	25.2	23.4	80.0	3.0	3.4
Commercial Sample B	59-67	33.1	18.2	80.9	3.0	10.5

TABLE 2.2A: EFFECT OF LIME CHARGE TO STAGE I ON DESILICATION OF LABORATORY GREEN LIQUOR AT 100°C, 15 MIN.

Run No.	CaO Per Cent	Stage I Liquor g/l		Caustici- zation		Desilication		SiO ₂ in Lime Mud Per cent
		NaOH	Na ₂ S	Na ₂ CO ₃	SiO ₂	Per cent	Per cent	
1	10	25.5	22.6	91.1	6.2	2.6	23.4	18.2
2	20	29.8	22.6	86.0	4.7	8.4	41.7	17.4
3	30	33.3	22.6	81.2	3.5	13.1	56.8	15.0
4	40	37.9	22.6	75.5	2.7	19.3	65.0	14.1
5	50	41.4	22.6	71.2	2.2	24.1	72.9	12.7
6	75	52.2	22.6	57.4	1.4	38.8	82.6	9.8
7	100	58.7	22.6	48.6	1.1	47.7	85.6	7.9

Green Liquor:		Sample 1500 ml	g/l
		Composition	
		NaOH	23.6
		Na ₂ S	22.6
		Na ₂ CO ₃	97.8
		SiO ₂	8.1
		Na ₂ SO ₄	3.0

TABLE 2.2B: EFFECT OF LIME CHARGE TO STAGE II ON CAUSTICIZATION
AND DESILICATION OF LABORATORY GREEN LIQUOR AT 100°C,
90 MIN.

Run No.	CaO Per cent	White Liquor, g/l			SiO ₂	Overall		SiO ₂ in Lime Mud Per cent
		NaOH	Na ₂ S	Na ₂ CO ₃		caustici- zation	Desili- cation	
						Per cent	Per cent	
1	90	78.5	22.6	26.2	0.6	74.5	90.2	6.7
2	80	74.5	22.6	25.1	0.5	69.1	88.5	5.6
3	70	75.0	22.6	27.2	0.4	69.6	87.0	4.7
4	60	74.0	22.6	30.2	0.6	68.4	77.5	3.9
5	50	69.6	22.6	33.3	0.8	62.4	62.2	3.0
6	25	68.8	22.6	36.4	1.1	61.4	21.4	1.3

STAGE I LIQUOR: SAMPLE 1000 ml

GREEN LIQUOR: COMPOSITION g/l

NaOH 23.6

Na₂S 22.6

Na₂CO₃ 97.8

SiO₂ 8.1

Na₂SO₄ 3.0

TABLE 2.3A: EFFECT OF LIME CHARGE TO STAGE I OL DESILICATION
OF LABORATORY GREEN LIQUOR AT 100°C, 30 MIN.

Run No.	CaO Per cent	Stage I Liquor g/l		SiO ₂	Caustici- zation Per cent	Desilication Per cent	SiO ₂ in Lime Mud Per cent
		NaOH	Na ₂ S				
8	10	27.1	22.6	90.6	6.2	4.7	23.4
9	20	31.0	22.6	85.5	5.0	10.0	17.4
10	30	35.6	22.6	79.7	3.2	16.2	38.2
11	40	38.7	22.6	73.8	3.0	20.5	60.2
12	50	43.7	22.6	66.6	2.5	27.2	63.1
13	75	57.4	22.6	50.7	1.1	45.8	68.5
14	100	69.6	22.6	33.3	0.8	62.4	85.5
							90.0
							7.9

Green Liquor:	Sample 1500 ml
Composition	g/l
NaOH	23.6
Na ₂ S	22.6
Na ₂ CO ₃	97.8
Na ₂ SO ₄	3.0

TABLE 2.3B: EFFECT OF LIME CHARGE TO STAGE II ON CAUSTICIZATION AND DESILICATION OF LABORATORY GREEN LIQUOR AT 100°C, 90 MIN.

Run No.	CaO Per cent	White Liquor, g/l		SiO ₂	Overall caustici- zation		Desili- cation		SiO ₂ in Lime Mud
		NaOH	Na ₂ S		Na ₂ CO ₃	Per cent	Per cent	Per cent	
8	90	79.0	22.6	22.0	0.7	75.0	89.0		6.5
9	80	81.0	22.6	20.5	0.3	77.8	93.6		6.1
10	70	81.2	22.6	17.9	0.1	78.0	98.0		4.6
11	60	73.2	22.6	27.7	0.2	67.4	95.0		5.0
12	50	68.8	22.6	28.2	0.6	61.3	76.1		4.2
13	25	72.4	22.6	30.6	0.8	66.0	29.9		1.5

Stage I Liquor Sample 100 ml

Green Liquor:	Composition	g/l
	NaOH	23.6
	Na ₂ S	22.6
	Na ₂ CO ₃	97.8
	SiO ₂	8.1
	Na ₂ SO ₄	3.0

TABLE 2.4A: EFFECT OF LIME CHARGE TO STAGE I ON DESILICATION
OF LABORATORY GREEN LIQUOR AT 100°C, 60 MIN

Run No.	CaO Per cent	Stage I Liquor g/l			Causticization per cent	Desilication per cent	SiO ₂ in Lime Mud per cent
		NaOH	Na ₂ S	Na ₂ CO ₃			
							SiO ₂

GREEN LIQUOR: Sample: 1500 ml

Composition		g/l
NaOH		23.6
Na ₂ S		22.6
Na ₂ CO ₃		97.8
SiO ₂		8.1
Na ₂ SO ₄		3.0

TABLE 2.4B: EFFECT OF LIME CHARGE TO STAGE II ON CAUSTICIZATION
AND DESILICATION OF LABORATORY GREEN LIQUOR AT 100°C,
90 MIN.

Run No.	CaO per cent	White liquor		g/l		overall caustici- zation per cent	Desili- cation per cent	SiO ₂ in Lime Mud per cent
		NaOH	Na ₂ S	Na ₂ CO ₃	SiC ₂			
15	90	78.2	22.6	21.4	0.7	73.4	90.1	6.5
16	80	78.0	22.6	22.3	0.3	73.7	91.6	5.6
17	70	78.0	22.6	22.3	0.2	73.7	92.0	4.4
18	60	78.2	22.6	22.5	0.4	73.4	81.8	3.3
19	50	78.6	22.6	23.1	0.6	74.2	69.0	3.0
20	25	79.0	22.6	23.6	0.7	75.2	19.6	0.8

Stage I Liquor: Sample 100 ml

Green liquor	Sample	Composition	g/l
	NaOH		23.6
	Na ₂ S		22.6
	Na ₂ CO ₃		97.8
	SiO ₂		8.1
	Na ₂ SiO ₄		3.0

TABLE 2.5A: EFFECT OF LIME CHARGE TO STAGE I ON DESILICATION
OF LAB. RECTORY GREEN LIQUOR AT 100°C, 90 MIN.

Run No.	Ca. per cent	Stage I Liquor		Caustici- zation per cent	Desili- cation per cent	Silica in Lime Mud per cent		
		NaOH	$\frac{\text{g/l}}{\text{Na}_2\text{CO}_3}$ Na_2S					
22	10	31.15	22.6	88.6	5.6	10.5	30.6	17.8
23	20	36.0	22.6	83.0	3.6	16.8	55.2	18.9
24	30	39.8	22.6	74.8	2.8	22.0	64.6	15.8
25	40	44.4	22.6	69.7	2.0	28.3	74.7	15.1
26	50	50.3	22.6	62.0	1.7	36.2	78.9	13.1
27	75	63.8	22.6	43.5	0.7	54.5	91.0	10.3
28	100	81.2	22.6	23.6	0.3	78.0	96.7	8.3

Green Liquor	Sample: 150C ml	
	Composition	g/l
	NaOH	23.6
	Na ₂ S	22.6
	Na ₂ CO ₃	97.8
	SiO ₂	8.1
	Na ₂ SO ₄	3.0

TABLE 2.5B: EFFECT OF LIME CHARGE TO STAGE II ON CAUSTICIZATION AND DESILICATION OF LABORATORY GREEN LIQUOR AT 100°C, 90 MIN.

Run No.	CaO per cent	White liquor			Overall caustici- zation per cent	Desili- cation per cent	SiC ₂ in Lime Mud per cent	
		NaOH	Na ₂ S	g/l Na ₂ CO ₃				SiC ₂
22	90	79.0	22.6	23.5	0.4	75.1	92.2	6.2
23	80	80.4	22.6	22.0	0.4	77.0	89.5	4.4
24	70	79.0	22.6	22.5	0.5	75.0	82.7	3.7
25	60	78.6	22.6	22.5	0.4	74.5	80.5	3.0
26	50	79.8	22.6	23.0	0.4	76.0	79.2	3.0
27	25	84.2	22.6	25.6	0.3	82.0	63.0	0.2

Stage I liquor Sample 1000 ml

Green Liquor	Composition	g/l
	NaOH	23.6
	Na ₂ S	22.6
	Na ₂ CO ₃	97.8
	SiO ₂	8.1
	Na ₂ SO ₄	3.0

TABLE 2.6: EFFECT OF REACTION TIME IN STAGE I ON DESILICATION OF
LABORATORY GREEN LIQUOR AT 130°C, 35 PER CENT LIME

Run No.	Time min	Stage I Liquor g/l			Caustici- zation per cent	Desili- cation per cent	SiO ₂ in Lime Mud per cent
		NaOH	Na ₂ S	Na ₂ CO ₃			
29	15	40.2	23.4	79.4	17.1	63.4	15.3
30	30	42.2	23.4	77.9	19.8	68.1	15.9
31	60	43.7	23.4	73.8	21.8	74.5	15.5
32	90	44.5	23.4	73.8	23.1	76.9	15.7
33	120	45.0	23.4	73.5	23.6	81.0	17.3

Green Liquor:	Sample Composition	1000 ml	
		g/l	
	NaOH	27.5	
	Na ₂ S	23.4	
	Na ₂ CO ₃	98.4	
	SiO ₂	8.0	
	Na ₂ SO ₄	3.0	

TABLE 2.7: EFFECT OF REACTION TIME IN STAGE I ON DESILICATION OF
LABORATORY GREEN LIQUOR AT 80°C, 35 PER CENT LIME

Run No.	Time min	Stage I Liquor I		SiO ₂	Causticization		Desilication		SiO ₂ in Lime M per cent
		NaOH	Na ₂ S	Na ₂ CO ₃	per cent	per cent	per cent	per cent	
34	15	35.6	23.4	83.0	3.7	10.9	54.0	13.7	13.7
35	30	38.3	23.4	81.4	3.0	14.5	62.4	15.4	15.4
36	60	40.2	23.4	75.3	2.6	17.1	68.1	15.5	15.5
37	90	42.1	23.4	74.6	2.5	19.7	69.0	15.7	15.7
38	120	43.3	23.4	73.2	1.7	21.3	78.5	16.9	16.9

Green liquor		Sample 1000 ml	
		Composition g/l	
		NaOH	27.5
		Na ₂ S	23.4
		Na ₂ CO ₃	98.4
		SiO ₂	8.0
		Na ₂ SO ₄	3.0

TABLE 2.8: EFFECT OF REACTION TIME IN STAGE I ON DESILICATION
OF LABORATORY GREEN LIQUOR AT 60°C, 35 PER CENT LIME

Run No.	Time min	Stage I Liquor g/l		Causticization per cent	Desilication per cent	SiO ₂ in Line mu per cent
		NaOH	Na ₂ S Na ₂ CO ₃			
39	15	30.2	89.1	3.0	34.5	9.5
40	30	32.5	87.5	6.7	42.3	11.3
41	60	34.0	85.0	8.8	46.7	12.1
42	90	35.6	82.9	10.9	61.5	15.3
43	120	37.2	80.4	13.8	65.4	15.9

Green liquor:		Sample 1000 ml	
		Composition	g/l
		NaOH	27.5
		Na ₂ S	23.4
		Na ₂ CO ₃	98.4
		SiO ₂	8.0
		Na ₂ SO ₄	3.0

TABLE 2.9: EFFECT OF LIME CHARGE TO STAGE I ON DESILICATION
OF COMMERCIAL GREEN LIQUOR AT 100°C, 30 MIN.

Run No.	CaO per cent	Stage I Liquor		SiO ₂	Caustici- zation per cent	Desilica- tion per cent	Silica in lime-mud per cent
		NaOH	Na ₂ S g/l				
44	10	29.8	71.3	3.3	7.6	2.9	5.5
45	20	35.0	64.4	3.0	16.5	12.4	8.3
46	30	39.6	67.2	2.8	23.5	17.8	6.9
47	40	44.0	52.5	2.5	31.1	26.9	7.2
48	50	51.0	43.2	2.4	42.7	28.8	6.8

Green liquor:	Sample: 1000 ml	
	Composition	g/l
	NaOH	25.2
	Na ₂ S	23.4
	Na ₂ CO ₃	80.0
	SiO ₂	3.4
	Na ₂ SiO ₄	3.0

TABLE 2.10: EFFECT OF LIME CHARGE IN STAGE I ON DESILICATION OF COMMERCIAL GREEN LIQUOR AT 100°C, 6 MIN

Run No.	CaO per cent	Stage I Liquor g/l		Causticization per cent	Desilication per cent	SiO ₂ in Lime Mud per cent
		NaOH	Na ₂ CO ₃			
49	10	31.6	73.5	10.6	10.3	8.5
50	20	37.2	66.3	19.8	16.2	8.1
51	30	44.0	69.4	31.1	29.0	8.4
52	40	48.4	51.4	38.4	39.6	8.2
53	50	53.8	44.3	47.6	46.0	8.0

Green Liquor:	Sample Composition	1000 ml g/l
	NaOH	25.2
	Na ₂ S	23.4
	Na ₂ CO ₃	80.0
	SiO ₂	3.0
	Na ₂ SO ₄	3.4

TABLE 2.11: EFFECT OF LIME CHARGE TO STAGE I ON DESILICATION OF COMMERCIAL GREEN LIQUOR AT 140°C, 90 MIN

Run No.	CaC per cent	Stage I Liquor g/l		Caustici- zation per cent	Desili- cation per cent	SiC ₂ in Lime Mud per cent
		NaOH	Na ₂ S Na ₂ CO ₃			
54	10	33.6	23.4 70.5	3.0 13.9	11.5	7.2
55	20	39.6	23.4 63.5	4.5 23.8	24.2	8.2
56	30	44.4	23.4 56.7	2.4 31.6	29.2	7.9
57	40	50.0	23.4 48.2	2.0 41.0	41.0	7.9
58	50	55.5	23.4 40.8	1.5 50.0	53.8	6.2

Green Liquor:		Sample	1000 ml
		Composition	g/l
		NaOH	25.2
		Na ₂ S	23.4
		Na ₂ CO ₃	80.0
		SiC ₂	3.4
		Na ₂ SC ₄	3.0

TABLE 2.12: EFFECT OF LIME CHARGE AND REACTION TIME ON
DESILICATION OF COMMERCIAL GREEN LIQUOR AT
100°C

Run No.	Time min	CaO per cent	Stage I Liquor		Caustici- zation per cent	Desilica- tion per cent	SiO ₂ in Lime Mud per cent
			NaOH	Na ₂ S Na ₂ CO ₃ g/l			
59	30	20	36.8	18.2 75.0	4.0 6.2	61.7	32.5
60	30	30	40.3	18.2 70.5	3.5 11.8	66.0	26.4
61	30	40	44.7	18.2 64.5	2.1 19.0	79.8	24.2
62	60	20	38.1	18.2 74.5	2.7 8.2	73.9	33.6
63	60	30	41.5	18.2 70.0	2.3 13.8	78.1	28.9
64	60	40	46.5	18.2 63.2	2.1 22.0	80.0	24.1
65	90	20	40.0	18.2 72.4	2.5 11.3	76.3	31.6
66	90	30	42.9	18.2 68.5	2.1 16.2	79.5	27.8
67	90	40	47.4	18.2 62.6	2.0 23.4	81.4	24.1

Green Liquor:	Sample	1000 ml
	Composition	g/l
	NaOH	33.1
	Na ₂ S	18.2
	Na ₂ CO ₃	80.9
	SiO ₂	10.5
	Na ₂ SO ₄	3.0

CHAPTER 3

PROCESS CALCULATIONS FOR PROPOSED GREEN LIQUOR DESILICATION PROCESS

3.1 MATERIAL AND ENERGY BALANCES:

Material and energy balances are given in Fig. 3.1, for a 250 tpd bamboo kraft pulp mill incorporating the two stage causticization concept for desilication of green liquor. A list of data and assumptions used in these calculations is summarised in Table 3.1. A balance for the amount of silica in the various process streams is given in Fig. 3.2 and Table 3.2, and the corresponding silica concentrations are given in Table 3.3. Table 3.4 summarises the composition and flow rates of the streams in double stage causticization for desilication of green liquor.

Digester house operations result in 110 m³/h of black liquor (20.4 per cent solids) containing 5.5 g SiO₂/l and the latter rises to 10.05 g SiO₂/l after processing through the multiple effect evaporators. The direct contact evaporator increases the concentration of the silica to 14.4 g/l in the black liquor fired to the recovery furnace. The molten smelt (Na₂CO₃ + Na₂S) from the recovery boiler will contain 8 per cent of the total sodium as silicate. The latter results in a concentration of 6.2 g SiO₂/l in the green liquor. The quantity of the green liquor to be processed

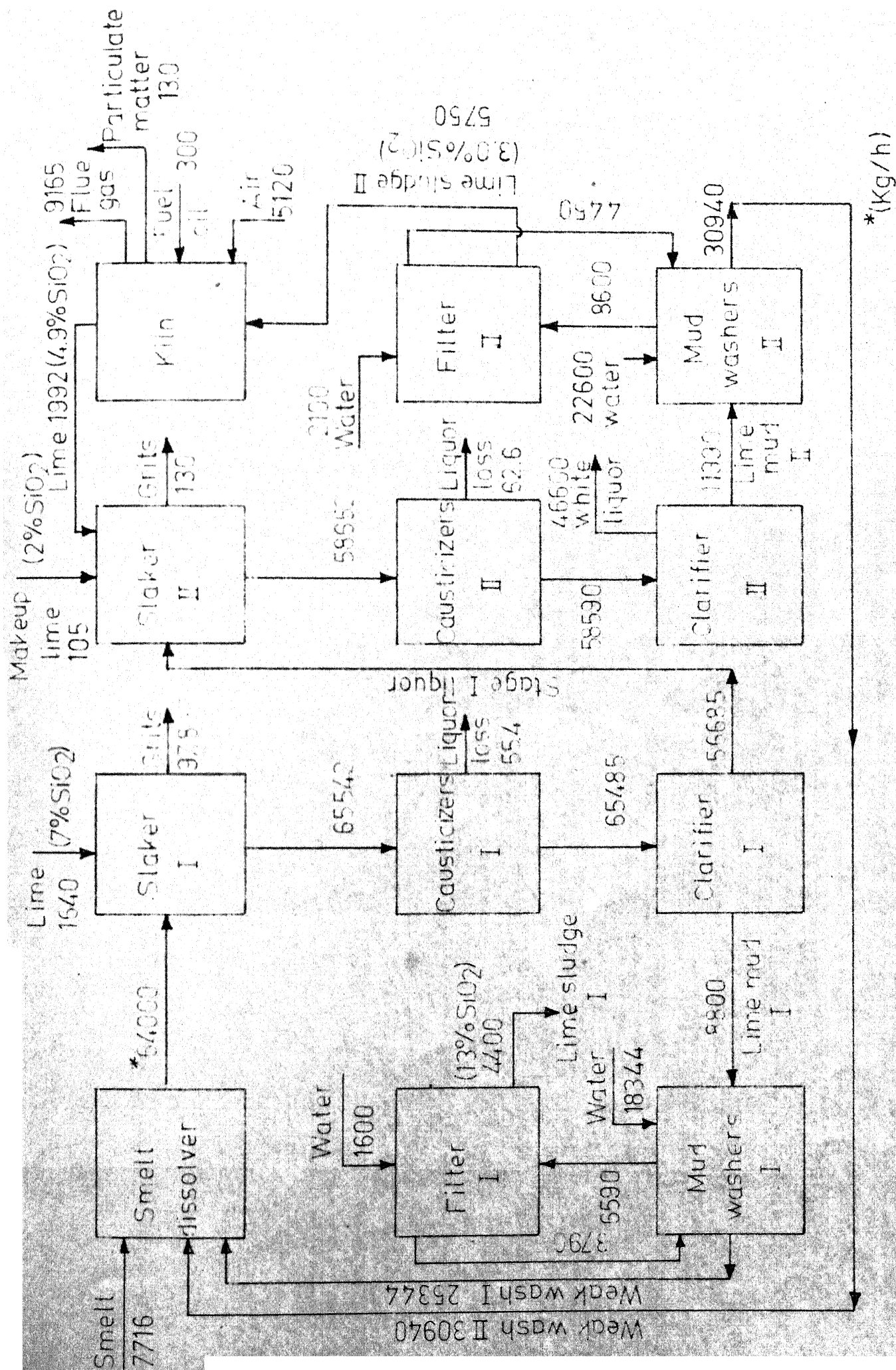


Fig. 3.1 - Material balances for desilication of green liquor by two stage causticization.

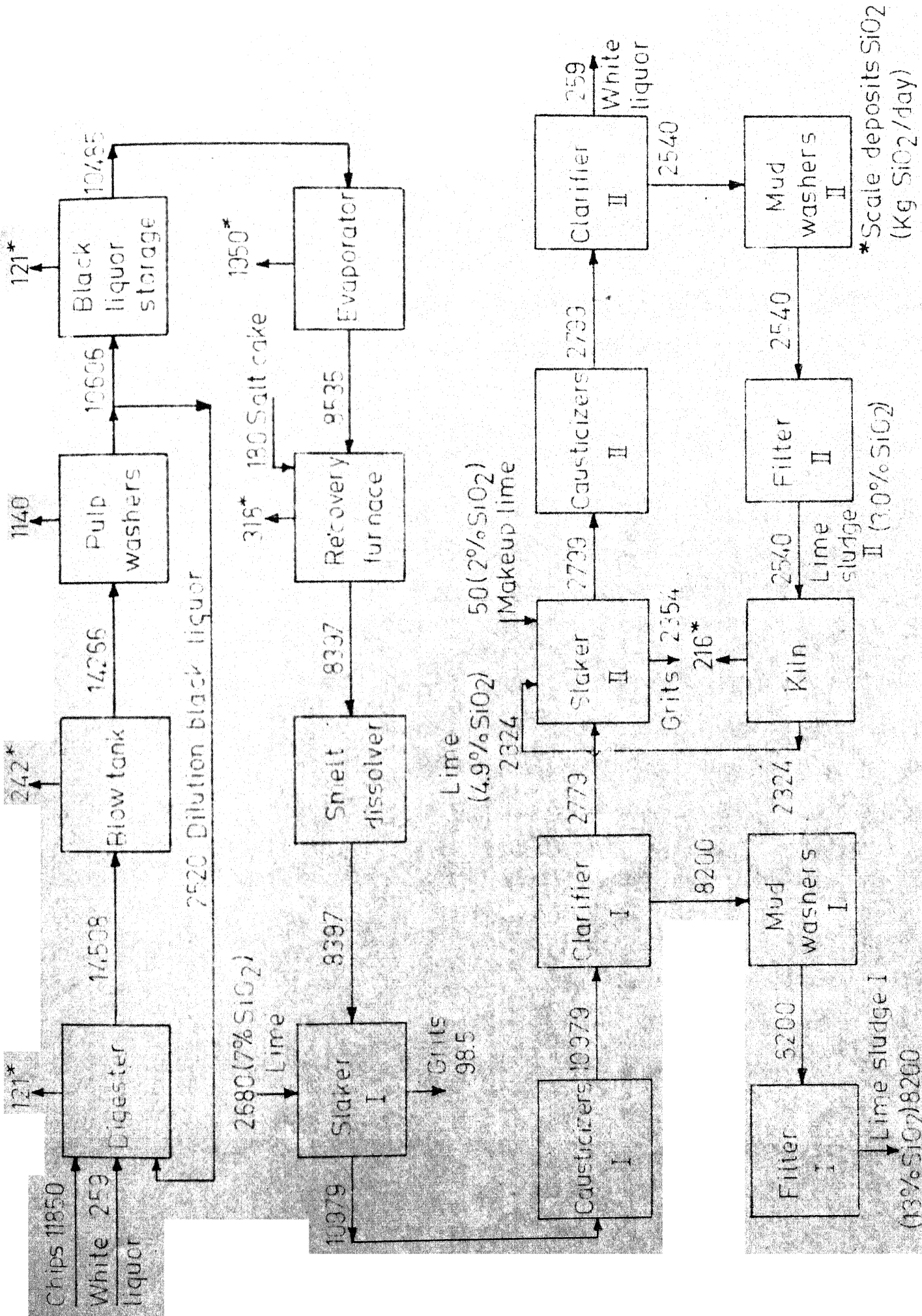


Fig. 3.2 -Silica balance for 250 TPD kraft pulp mill with green liquor desilication by two stage causticization

for desilication will be $58.0 \text{ m}^3/\text{h}$. The components in green liquor consists of Na_2CO_3 (104.5 g/l), NaOH (17.2 g/l), Na_2S (21.4 g/l), Na_2SO_4 (2.1 g/l) and Na_2SiO_3 (12.6 g/l). The usual causticization reactions will require 5.35 t/h of lime. Conventional pulp mills will dispose of the 12.0 t/h of lime sludge containing 7.7 per cent SiO_2 and use fresh lime in once through operation. However the two stage causticization technique of this study necessitates the addition of 30 per cent lime to the stage I (1.64 t/h) and the lime sludge produced (4.40 t/h) from stage I will contain 13 per cent SiO_2 , assuming an initial silica content of 7 per cent SiO_2 for the lime used in causticization and a desilication efficiency of 65 per cent. Sludge from stage I will be discarded. The first stage liquor will have NaOH (43 g/l), Na_2CO_3 (85.5 g/l), Na_2S (22.8 g/l), Na_2SO_4 (2.15 g/l) and SiO_2 (2.29 g/l). Sodium carbonate in the green liquor is partially causticized (23 per cent) during desilication in stage I, causticization reactions are completed in stage II by using the reburned lime 2.0 t/h along with make up lime 0.1 t/h. Makeup lime will have 70 per cent CaO , 2 per cent SiO_2 , 28 per cent inerts. Stage II yields a causticization efficiency 80 per cent and the lime sludge with 3.0 per cent SiO_2 .

Stage I and Stage II produce 4.4 t/h and 5.75 t/h of lime sludge respectively. Lime sludge from the both

stages are sent to a separate system of clarifier (for separation of liquor from sludge), mud washers (for alkali recovery) and rotary drum filters (for alkali recovery). Stage II lime mud will contain 0.18 per cent residual alkali (as Na_2O) and is calcined in a kiln and reburned lime with 4.9 per cent SiO_2 is recycled to slaker II together with makeup lime 0.1 t/h (2 per cent SiO_2). Wash water requirements in stage I and stage II will be 19.9 and 25.8 t/h respectively. Weak wash liquor from these stages is used for dissolving the smelt. Lime kiln requires 0.3 t/h of fuel oil (calorific value 10700 Kcal/kg).

TABLE 3.1: SUMMARY OF DATA AND ASSUMPTIONS FOR
MATERIAL AND ENERGY BALANCE CALCULATIONS

Basis: 250 tpd bamboo kraft pulp mill:

1. Bamboo Chips:

Silica, per cent SiO_2	2.1
Ash, per cent	1.0
Moisture, per cent	40.0
Specific heat	0.35
Elemental composition, per cent	
C=50.0, H=6.0, O=44.0.	

2. White Liquor: (Chemicals are expressed as equivalent Na_2O)

Sulphidity per cent $\text{Na}_2\text{S}/(\text{NaOH}+\text{Na}_2\text{S}) \times 100$	20.0
Activity per cent $\text{Na}_2\text{S}+\text{NaOH}/(\text{NaOH}+\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3+\text{Na}_2\text{SO}_4) \times 100$	83.5
Reduction per cent $\text{Na}_2\text{S}/(\text{Na}_2\text{S}+\text{Na}_2\text{SO}_4) \times 100$	95.0
Strength, Kg/m^3 Active alkali Kg/m^3	90.0
Specific gravity	1.08
Specific heat	0.91
Temperature, $^{\circ}\text{C}$	90.0

Composition (g/l as Na_2O)

NaOH 72.0	Na_2S 18.0	SiO_2 0.12
Na_2CO_3 13.6	Na_2SO_4 0.95	

3. Batch Digesters:

Heating arrangement	- Open steam and external heater
Chemical charge, per cent as Na_2O	17.0

Liquor to wood ratio	3.5:1.0
Degree of delignification, per cent	92.0
Pulping temperature, °C	170.0
Digester pressure, Kg/cm ²	9.0
Steam pressure, Kg/cm ²	8.2
Unbleached pulp yield, per cent	50.0
Heat loss, (per cent total heat input)	5.0
Digester relief (per cent o.d. chips)	3.5

4. Blow Tank:

Operating pressure, atm	1.0
Heat loss (per cent of heat input to digester)	0.5

5. Brown Stock Washers:

Number of washers	3.0
Washed pulp consistancy, per cent	12.0
Alkali loss, Kg Na ₂ SO ₄ per ton of pulp	18.0
Dilution factor	3.0

6. Weak Black Liquor:

Concentration, per cent	18.05
Specific heat	0.91
Specific gravity	1.11
Temperature, °C	90

7. Multiple Effect Evaporator:

Number of effects	6.0
Steam economy	4.75
Strong black liquor, per cent	50.0

3. Direct Contact Evaporator and Recovery Furnace:

Concentration of strong black liquor, per cent	65.0
Specific heat of black liquor (65 per cent)	0.65
Particulate matter in flue gas Kg/ton of pulp (95 per cent Na_2CO_3 , 5 per cent Na_2SO_4)	17.0
Inlet air temperature, $^{\circ}\text{C}$	30.0
Inlet air humidity, per cent	60.0
Excess air, per cent	20.0
Composition of the black liquor solids	Per cent
Na	17.10
S	1.67
C	35.80
O	40.10
H	4.45
Si	<u>0.85</u>
Total	<u>100.00</u>
Smelt composition (per cent of total Na)	
Na_2S	17.40
Na_2SO_4	0.89
Na_2CO_3	73.80
Na_2SiO_3	<u>7.91</u>
Total	<u>100.00</u>

Causticization

(alkali loss expressed as Kg of Na_2O per ton of pulp).

Alkali loss in stage I with grits	0.4
Alkali loss in stage II with grits	0.5

Slaker grits in stage I, kg/ton of pulp	5.0
Slaker grits in stage II, kg/ton of pulp	9.6
Alkali loss in stage I causticizers	0.5
Alkali loss in stage II causticizers	0.57
Retention time in stage I slaker, min	20.0
Retention time in stage I causticizers, min	70.0
Lime added to stage I, per cent of theoretically required	30.0
Desilication efficiency in stage I, per cent	65.0
Causticization efficiency in stage I, per cent	23.0
Retention time in stage II slaker, min	30.0
Retention time in stage II causticizers, min	90.0
Desilication efficiency in stage II, per cent	82.0
Causticization efficiency in stage II, per cent	80.0
Stage I clarifier underflow solids, per cent	30.0
Stage II clarifier underflow solids, per cent	32.0
Underflow solids in stage I and stage II mud washers, per cent	40.0
Lime sludge from stage I and stage II filters, per cent	60.0
Alkali loss with stage I lime sludge	1.73
Alkali loss with stage II lime sludge	0.96

Lime Kiln:

Type		Rotary
Gross calorific value of fuel oil, Kcal/kg		10,700.0
Excess air for combustion, per cent		20.0
Composition of fuel oil, per cent		
C	86.20	
H	12.39	
S	0.39	
Ash	0.69	
H ₂ O	<u>0.33</u>	
Total	<u>100.00</u>	

TABLE 3.2: SILICA BALANCE FOR 250 TCN/DAY BAMBOO
KRAFT PULP MILL^δ

INPUT			OUTPUT		
Source	Conven- tional	Modi- fied	Source	Conven- tional	Modi- fied
Bamboo chips	11850 ^δ	11850	Scales		
White liquor	3000	259	Digester	172	121
Makeup salt cake	180	180	Blow tank	345	242
Makeup lime	8240	2730	Black liquor storage tank	172	121
			Evaporators	2740	1950
			Recovery furnace	452	318
			Lime kiln	-	216
			Washed pulp	1620	1140
			Slaker grits	3140	2452
			White liquor	3000	259
			Lime sludge	11628	-
			Stage I lime mud	-	8200
Total	23270	15019	Total	23269	15019

^δKg per day

TABLE 3.3: SILICA CONCENTRATIONS IN VARIOUS PULP
MILL LIQUOR STREAMS

Stream	Conventional recovery	Recovery with desilication of green liquor
Chips, per cent SiO_2	2.10	2.10
Weak black liquor, g SiO_2 /l	5.33	4.41
Strong black liquor, g SiO_2 /l	12.50	10.05
Green liquor, g SiO_2 /l	7.54	6.20
White liquor, g SiO_2 /l	2.90	0.25
Lime sludge, per cent SiO_2	7.70	-
Stage I lime mud, per cent SiO_2	-	13.00
Stage II lime mud, per cent SiO_2	-	2.98
Reburned lime, per cent SiO_2	-	4.85
Fresh lime, per cent SiO_2	7.00	-
Fresh lime to stage I, per cent SiO_2	-	7.00
Makeup lime to stage II, per cent SiO_2	-	2.00

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TABLE 3.4: COMPOSITION AND FLOW RATES OF STREAMS IN
DOUBLE STAGE CAUSTICIZATION SECTION FOR
DESILICATION OF GREEN LIQUOR

Stream	Flow rate		Composition, g/l				
	m ³ /h	Kg/h	NaOH	Na ₂ S	Na ₂ CO ₃	Na ₂ SO ₄	SiO ₂
Green liquor	58.00	64,000	17.20	21.40	104.50	2.10	6.20
Stage I liquor	51.00	56,685	43.00	22.80	85.50	2.15	2.28
Stage I lime mud waste	3.14	4,400	2.37	1.26	4.70	0.12	0.12
Stage II lime sludge to kiln	4.10	5,750	2.26	0.52	0.40	0.50	0.06
White liquor	42.00	46,600	99.50	23.00	17.60	2.21	0.25

3.2 PROCESS EQUIPMENT DESIGN:

The following additional equipment will be necessary in the proposed modified causticizing operations with desilication accomplished in the first stage; slaker, causticizers (2), clarifier, mud washers (2), mud filter and rotary lime kiln.

Process design calculations are based on green liquor flow rate of $58 \text{ m}^3/\text{h}$ and with the following composition (g/l as chemical)

Na_2CO_3 :	104.5	Na_2SO_4 :	2.1
Na_2S :	21.5	SiO_2 :	6.2
NaOH :	17.2		

Slaker and Causticizers:

Capacity of the slaker and causticizers are calculated on the basis of the retention time of 20 min, and 70 min respectively.

Clarifier:

A two tray thickner is used for separating lime mud from the stage I liquor. The area of the clarifier is estimated based on the results of the batch settling experiment [4]. Batch data is used to calculate the minimum velocity of lime mud and settling velocity (V_L), concentration (C_L) is calculated using equations 3.1 and 3.2 [5].

$$V_L = (dz/dt)_{Z_i} \quad (3.1)$$

$$C_L = C_o \times Z_o/Z_i \quad (3.2)$$

A graph of V_L vs $V_L/(1/C_L - 1/C_u)$ (ρ_{av}/g) gives the minimum settling velocity of the lime mud particles. Using this minimum velocity, clarifier cross section is computed from equation 3.3 [6].

$$A = 1.33 \times F - U/R \times S \quad (3.3)$$

Volume of the clarifier is calculated by equation 3.4 [6].

$$V = 4 T(G-S)/3G(S_g - S) \quad (3.4)$$

Mud Washers:

Volume of each mud washers (2 units) is taken to be equal to that of the stage I clarifier [7].

Mud Filter:

Rotary vacuum drum filter is used for the recovery of liquor retained in lime sludge. Standard sizes for such filters are given by Purchas [8] for different capacities. Filter area is based on capacity of the filter and lime mud flow rate. Length and diameter of the filter is computed on the basis of area [6].

Lime Kiln:

Lime sludge is calcined in a rotary kiln of which the standard size of diameter is computed for a given capacity [9] and the length of kiln is calculated by using the equation 3.5 [6].

$$\text{Tons of lime product/day} = k L D^2/100 \quad (3.5)$$

The total kiln length is distributed as 12.0, 29.0, 18.0, and 41.0 per cent of the total length for the cooling,

calcination, preheating and drying zones respectively [10].

Retention time of lime in the kiln is calculated [9] by using the equation (3.6)

$$T = M L / \dot{C} N D \quad (3.6)$$

Equipment Design Specification:

a. Slaker

Retention time, min	20.0
Capacity, m ³	18.2
Diameter, m	3.0
Height, m	2.6

b. Causticizers:

Number	2
Retention time, min	70.0
Capacity, m ³	63.7
Diameter, m	3.0
Height, m	4.5

c. Clarifier:

Type: Multicompartment tray thickner	
Number of trays	2
Diameter, m	10.8
Height, m	4.8

d. Mud Washers:

Number of mud washers	2
Diameter, m	10.8
Height, m	4.8

e. Mud filter:

Type:	Rotary drum filter
Solids flow rate, Kg/h	2638.0
Filtration capacity, Kg/h m ²	585.0
Filter area, m ²	4.6
Length, m	1.2
Diameter, m	1.2
Speed, rpm	1.0

f. Lime kiln:

Type:	Rotary Kiln
Lime sludge, t/h	5.7
Moisture in lime sludge, per cent	40.0
Lime production, t/h	2.0
Available CaO, per cent	92.0
Fuel oil, Kg/h	300.0
Air, Kg/h	5120.0
Diameter, m	1.5
Length, m	60.0
Cooling zone, m	7.0
Calcination zone, m	17.6
Preheating zone, m	10.6
Drying zone, m	24.7
Speed of rotation, rpm	1.0
Inclination, degree	2.4
Retention time, min	175.0
Horse power, hp	40.0

Type of driving: Motor with girth gear
 Number of supports 4

3.3 COST ESTIMATION:

A bulgetary estimates of the capital requirement for the additional equipment in the proposed process for desilication of green liquor is given in Table 3.5, and the operating cost is given in Table 3.6.

The total capital investment is about Rs.49,50,000 and the operating cost per day is about Rs.21,835. Net daily saving of the proposed process will be the difference in the cost of fresh lime in conventional process and the operating costs of the new process. Daily savings come to about Rs.3,765 and the saving per ton of pulp is Rs.15/-. A 26 per cent of rate of return only will be obtained from the proposed process.

TABLE 3.5: ESTIMATION OF CAPITAL REQUIREMENT FOR MODIFIED PROCESS

S.No.	Item	Number	Unit Cost Rs	Total Cost Rs
1.	Slaker	1	2,00,000	2,00,000
2.	Causticizers	2	50,000	1,00,000
3.	Mud washers	2	2,00,000	4,00,000
4.	Mud filter	1	4,00,000	4,00,000
5.	Line kiln	1	20,00,000	20,00,000
6.	Pumps, pipe lines and accessories (7.5 per cent of equipment cost)	-	-	2,00,000
7.	Construction, instrumentation and insulation (50 per cent of equipment cost)	-	-	16,50,000
Total investment				49,50,000

Basis: 58 m³/h of green liquor in a 250 tpd
Bamboo kraft pulp mill

TABLE 3.6: ESTIMATION OF OPERATING COST FOR
MODIFIED PROCESS

S.No.	Item	Amount	Unit Price Rs.	Total Cost Rs.
1.	Fuel oil, t	7.2	1000	7200
2.	Lime for stage I, t	39.4	200	7880
3.	Makeup lime for stage II, t	2.52	300	755
4.	Power, KWH	4000	0.25	1000
5.	Labour and supervision	-	-	1000
6.	Maintenance	-	-	1000
7.	Depreciation, taxes and insurance (20 per cent of fixed capital investment)	-	-	3000
Total operating cost				21,835

Basis: One day of operation

CHAPTER 4

SUMMARY AND RECOMMENDATIONS

Silica entering the chemical recovery system through bamboo chips, lime and salt cake results in 5-20 per cent SiO_2 in lime mud, unsuitable for efficient calcining and is discarded. This study proposes a modified two stage causticizing step for the preferential desilication of green liquor. The first stage using 25-30 per cent of lime requirement removes two thirds of the silica in green liquor and sludge from second causticizing stage containing 3-4 per cent SiO_2 can be calcined in a rotary kiln.

The effects of temperature, time and lime charge and silica concentration on desilication efficiency of green liquor is studied. The results show that as the temperature, reaction time, and lime charge is increased in stage I, desilication efficiency increases. Increase in lime addition (10-100 per cent) increases desilication efficiency from 30 to 97 per cent at 100°C , and 90 min. in stage I. Increase in reaction time (15-90 min), increases desilication efficiency from 51 to 66 per cent at 100°C , and 30 per cent lime charge in stage I. Increase in temperature ($60-100^\circ\text{C}$), increases desilication efficiency from 61 to 78 per cent at 90 min., and 35 per cent lime charge in stage I. Increase in temperature and time increases silica content in lime mud,

savings of Rs. 15 per ton of pulp will be obtained. The rate of return will be about 26 per cent by this modified process.

The major advantage of this modified process over that of the carbonation process [2] is that the capital investment and operating cost are lower. In the carbonation process the capital investment is about Rs.60,00,000 and operating cost is about Rs.35,000. This high operating cost is due to the high steam requirement 500 t/d at about Rs.50/t and requirement of more power for the turbulent contact absorber. The high capital investment is due to the stripping column of Rs.18,00,000. Further turbulent bed absorber is a relatively new type of gas-liquid contacting equipment requiring substantial development work.

Additional equipment required for the process proposed in this study are readily available from companies like Dorr-Oliver, Bombay, Utkal Machinery, Orissa, and Eimco-KCP; Madras. Pilot plant investigations are necessary especially for evaluating the calcination characteristics of stage II lime sludge. Some paper mills do have spare equipment available for mill scale trials of the proposed process. The results of this study show potential promise of commercial applicability of the two stage causticization concept for desilication of kraft green liquor.

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APPENDIX

DESIGN OF STAGE I CLARIFIER AND ROTARY LIME KILN

Stage I Clarifier:

Cross section of the clarifier is computed by calculating the minimum velocity from the batch settling test data. The minimum velocity is found by calculating V_L and C_L from equations 3.1 and 3.2, and a plot of V_L vs $V_L / [(\frac{1}{C_L} - \frac{1}{C_u}) \frac{s_{av}}{s}]$. Area of the clarifier is given by equation 3.3, and the equation 3.4 gives the necessary volume of the clarifier.

Basis: One hour

Stage I liquor and lime mud flow rate, Kg	65,485.0
Stage I liquor and lime mud flow rate, m ³	54.5
Lime mud flow rate, Kg	2638.0
Lime mud feed concentration, Kg/m ³	48.5
Initial height of the slurry in settling test cylinder, cm	33.0

Experimental Data:

Settling curve for stage I lime mud is given in Fig.A.1 (based on batch experiment in a one liter measuring cylinder). Table A.1 is prepared based on this graph (A.1).

Values of V_L and C_L from Table A.1 are used to get Fig. A.2, which represents the underflow concentration as 300 Kg/m³. The last two columns of the Table A.2 are plotted

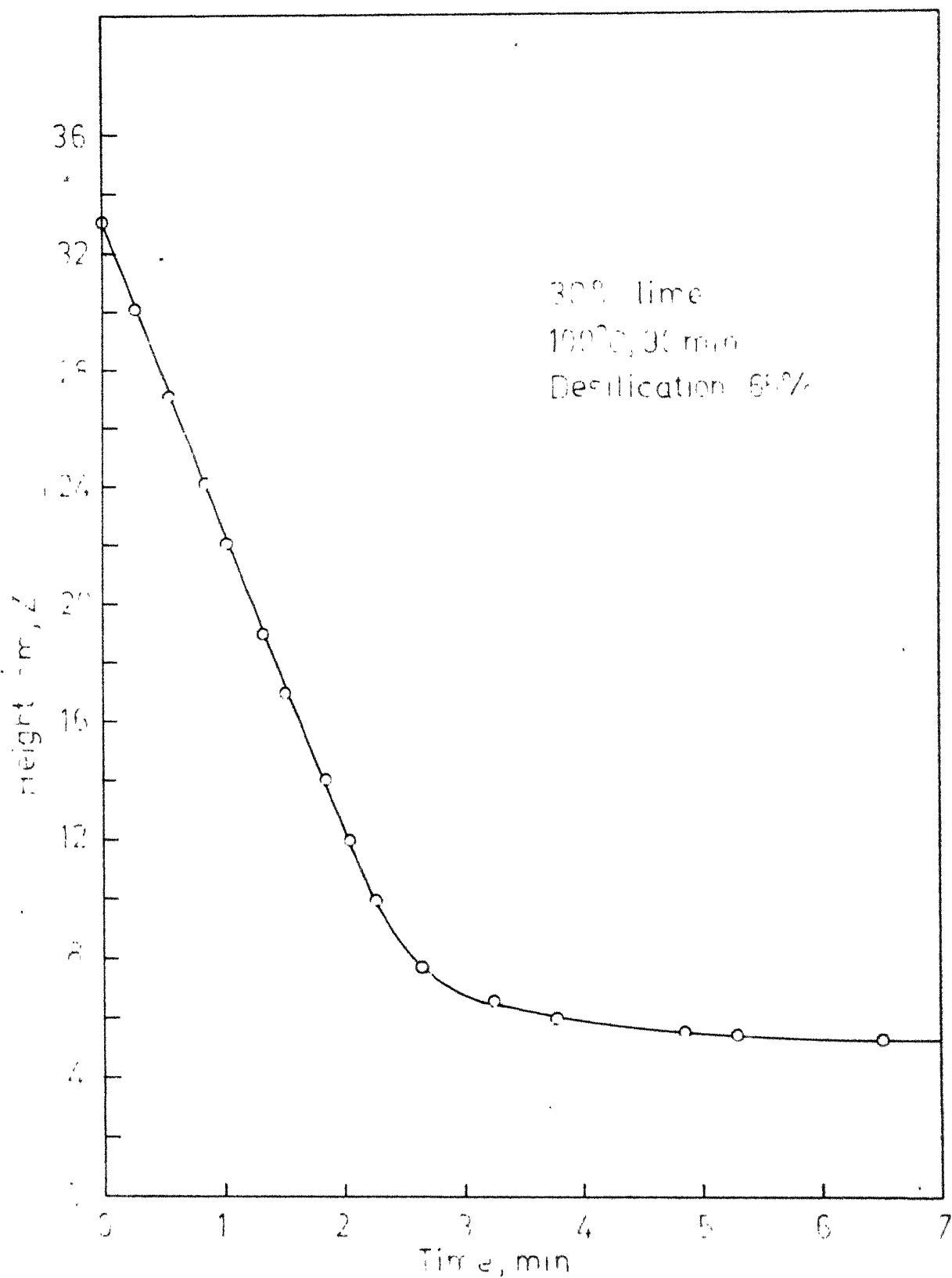


Fig.A.1 - Settling rate of stage I lime mud using commercial green liquor.

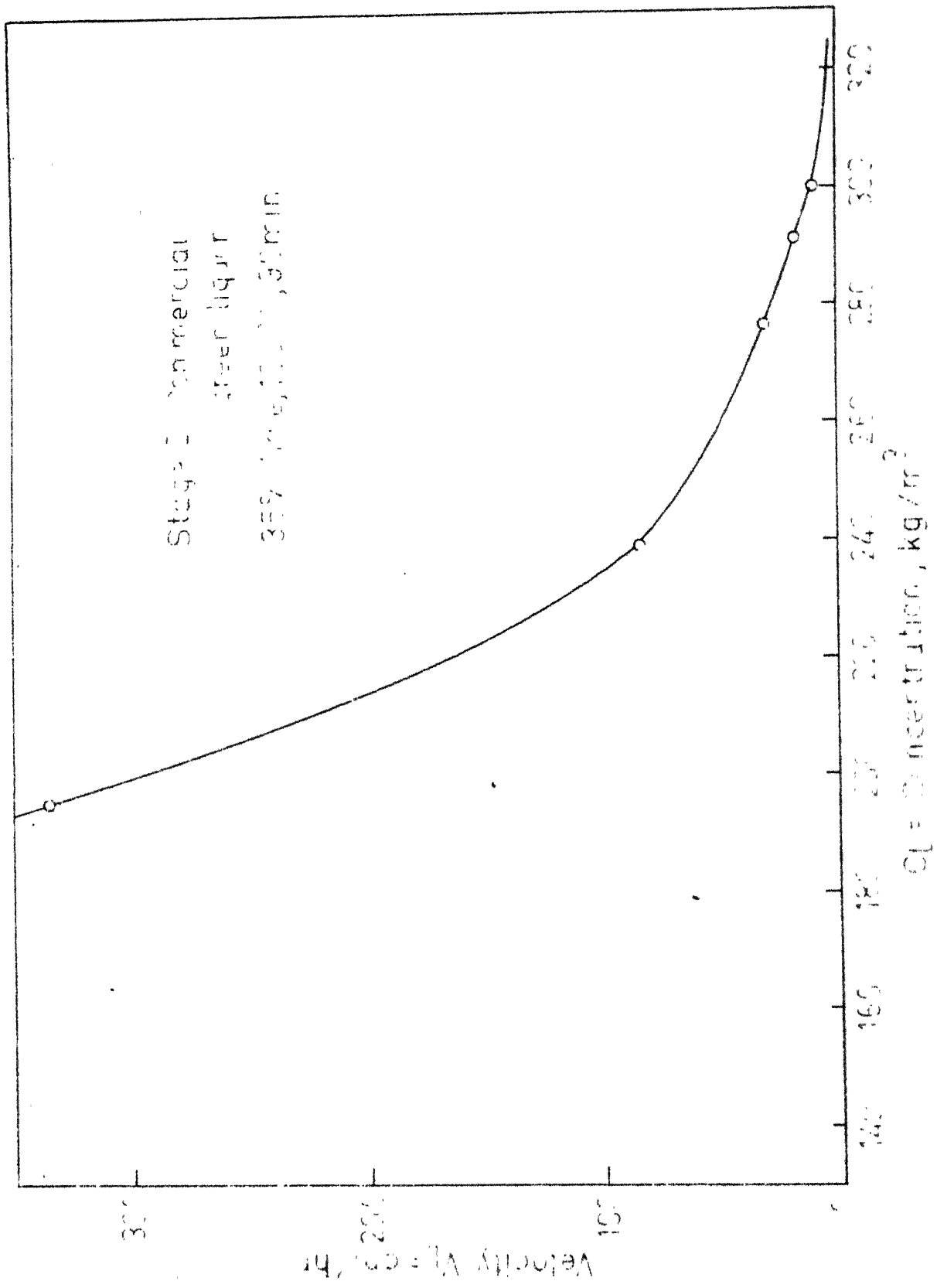


Fig A.2 - Settling velocity vs. solid concentrations in commercial green liquor

TABLE A.1: SETTLING VELOCITY (V_L) AND CONCENTRATION (C_L) FROM SETTLING CURVE FOR COMMERCIAL GREEN LIQUOR IN STAGE I

S.No.	Z cm	V_L cm/h	C_L Kg/m ³
1	12.0	600.0	133.5
2	8.2	336.0	195.0
3	6.7	83.0	239.0
4	5.8	30.0	276.0
5	5.5	14.4	291.0
6	5.4	7.2	297.0

TABLE A.2: FINDING THE MINIMUM VELOCITY TO CALCULATE
THE CROSS SECTION OF THE CLARIFIER

S.No.	V_L cm/h	C_L Kg/m ³	$1/C_L - 1/C_u$ m ³ /kg	$[1/C_L - 1/C_u]$ m ³ /kg	$V_L / (1/C_L - 1/C_u)$ x $\frac{g}{g}$ cm/h x Kg/m ³
1	200	215	.00132	.00143	14.0 x 10 ⁴
2	100	235	.00092	.000996	10.0 x 10 ⁴
3	50	260	.00052	.000564	8.8 x 10 ⁴
4	25	282	.00021	.000228	10.9 x 10 ⁴
5	15	290	.00012	.000121	12.3 x 10 ⁴

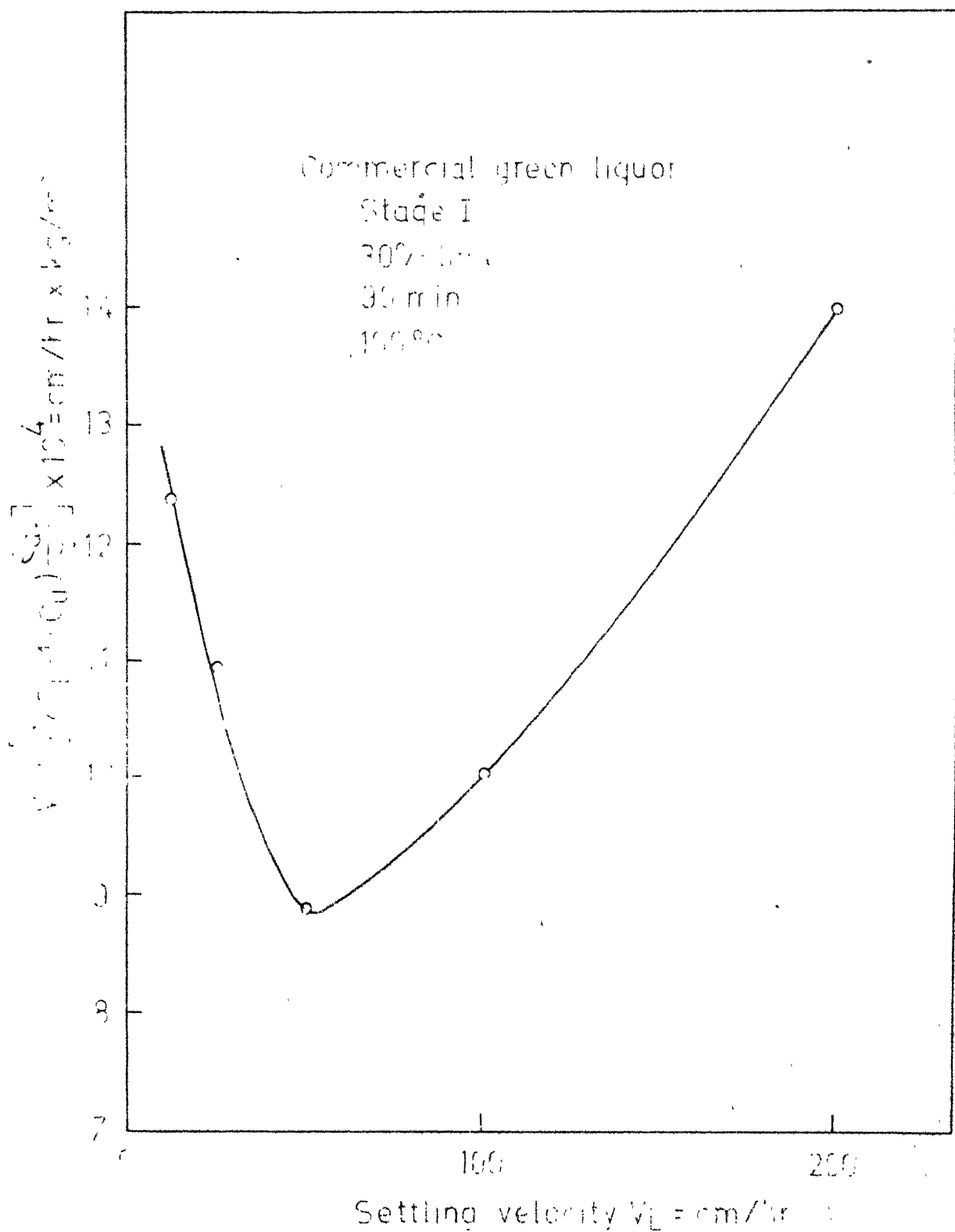


Fig: A.3 - Plot of $V_L / \left[\left(\frac{1}{C_L} - \frac{1}{C_U} \right) \frac{\epsilon_{av}}{V_L} \right]$ vs. settling velocity for determining minimum velocity.

in Fig. 4.3 and from which the minimum velocity is computed to be 50 cm/h

$$\text{Cross section of clarifier} = A = 1.33 \times F \cdot U / R \times S$$

$$F = 23.8$$

$$R = 50 \text{ cm/h}$$

$$U = 2.34$$

$$S = 1.1$$

$$A = 930 \text{ m}^2$$

$$\text{Diameter} = 10.8 \text{ m}$$

$$\text{Volume of clarifier} = V = 4 T [G - S] / 3G [S_s - S]$$

$$T = 30 \text{ h}$$

$$S = 1.1$$

$$G = 2.93$$

$$S_s = 1.3$$

$$V = 2240 \text{ m}^3$$

$$\text{Height} = 2.4 \text{ m}$$

$$\text{Total height (for a two tray unit)} = 4.8 \text{ m}$$

$$D = 10.8 \text{ m}$$

$$H = 4.8 \text{ m}$$

Lime Kiln: Basis: One hour

Lime sludge flow rate, Kg	5740.0
Water, Kg	2311.2
Lime mud, Kg	3446.0
Dissolved solids, Kg	13.8
Lime mud feed temperature, °C	30.0
Product lime temperature, °C	650.0
Inlet air temperature, °C	30.0
Exit flue gas temperature, °C	150.0
Lime discharge, tpd	47.8
Diameter, m	1.5

$$\text{Capacity} = \pi D^2 L / 100$$

$$D = 1.5 \text{ m}; K = 1.0$$

$$h = 60 \text{ m.}$$

Total heat required:	Kcal
Heat required in evaporation of residual moisture	13,43,750
Heat of dissociation CaCO_3	15,00,000
Heat of dissociation Ca(OH)_2	1,000
Enthalpy of lime at 650°C	3,03,000
Enthalpy of flue gas at 150°C	78,108
Total	<u>32,15,858</u>

$$\text{Calorific value Kcal/kg} = 10,700$$

$$\text{Fuel oil required} = 32,15,858 / 10700$$

$$\text{Fuel oil required} = 300 \text{ Kg}$$

$$\text{Oxygen required} = [\text{For combustion} + \text{Excess Oxygen}]$$

$$\text{Oxygen required} = 1185 \text{ Kg}$$

$$\text{Air required} = 1185 / 232 = 5120 \text{ Kg}$$

$$\text{Fuel oil required} = 300 \text{ Kg}$$

Air required = 5120 Kg	% of total length	Length m
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Cooling zone.	12.0	= 7.0
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Calcination zone	29.0	17.6
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Preheating zone.	18.0	10.6
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Drying zone.	41.0	24.7
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Kiln length	<u>100.0</u>	<u>60.0</u>
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Horse power, hp	40.0
Number of supports	4
Type of driving	Motor with girth gear
Rotations, rpm	1
Angle of inclination, degree	2.4

Retention time of lime in kiln [6] is calculated by the equation 3.6.

$$T = ML / \pi ND$$

$$M = 10.5 \quad : \quad \theta = 2.4 \quad D = 1.5$$

$$L = 60 \text{ m} \quad : \quad N = 1.0$$

$$T = 175 \text{ min}$$

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